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NAPHTHA HYDROFINING TO REMOVE NITROGEN

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This invention relates to processes for hydrofining naphtha, and more particularly it relates to processes for catalytic hydrogenation of nitrogen compounds contained in gasoline boiling range feeds to prepare a feed of low nitrogen content for a catalytic reforming process wherein the gasoline octane number is to be increased.

Catalytic reforming of gasoline-boiling-range, or naphtha, hydrocarbons to produce high octane gasoline is well known. The most common process comprises contacting such a naphtha feed with a halided platinum-alumina reforming catalyst at elevated temperatures of above 850° F. and pressures above 200 p.s.i.g. in the presence of hydrogen. The platinum catalysts are deactivated or poisoned by nitrogen compounds if present in the feed. Accordingly, the most common process is the so-called two-stage process wherein the naphtha feed to be reformed is first hydrofined by contacting with a sulfactive hydrofining catalyst, such as supported cobalt-molybdenum, to remove nitrogen compounds by converting them to ammonia. With increasing demands for greater quantities of higher octane gasoline, it is desired to increase the throughput in existing processes of this type, particularly during interim periods when product demand exceeds existing plant capacity but not by enough to justify the construction of additional facilities.

In the existing hydrofining processes for preparing catalytic reformer feed, the operating conditions are dictated by the daily naphtha throughput in combination with the concentration of nitrogen compounds in the naphtha feed and the need to convert to ammonia all nitrogen compounds in the naphtha feed in excess of a specified maximum nitrogen content for catalytic reformer feed. Generally, the maximum permitted nitrogen content in catalytic reformer feed is below 1 p.p.m. total nitrogen, for example 0.5 p.p.m. N. The naphtha may contain 20–1000 p.p.m. N, more usually 100–300 p.p.m. N. Because the maximum operating pressure is set by design, attempts to increase daily naphtha throughput with a feed of given nitrogen content necessitate using a higher temperature, as this is the only remaining adjustable process variable to convert nitrogen compounds more rapidly. The higher temperature results in more rapid catalyst fouling creating a need for more frequent catalyst regeneration.

The present invention is directed to the problem of increasing the throughput of existing hydrofining processes of the described class without decreasing the on-stream time between catalyst regenerations.

Recently catalysts which are much more active for the specific purpose of hydrogenating nitrogen compounds contained in hydrocarbon oils to ammonia have been discovered. For example, the use of such catalysts is disclosed and claimed in U.S. Patent 3,114,701 to Robert L. Jacobson and Robert H. Kozlowski. Therein it is disclosed that sulfided nickel-molybdenum-alumina catalysts containing 4%–10% nickel and 15.5%–30% molybdenum are several times more active for hydrodenitrification than previously known hydrofining catalysts. Specifically, catalysts containing at least about 4% nickel

and at least about 19% nickel are more than 3.5 times as active as the conventional cobalt-molybdenum-alumina catalysts which had been in use in processes for removing nitrogen compounds from naphtha for more than ten years previously.

Within the old class of hydrofining catalysts exemplified by cobalt-molybdenum are many catalysts of different composition, including nickel-tungsten and low metal content nickel-molybdenum, which differ in activity to some degree. It should be noted, however, that activity differences of up to 10% have little practical commercial significance because the hydrofining processes are not built and operated with such precision as to take advantage of such a small difference. Accordingly, selection of a catalyst among several alternatives is made primarily on the basis of price, unless one catalyst is much more active than the others, e.g. by a factor of whole numbers.

In U.S. Patent 3,114,701 it is disclosed that naphtha of given nitrogen content can be completely denitrified by passing with hydrogen downflow through a fixed bed of high nickel-and-molybdenum content catalyst at 600° F. and 800° p.s.i.g. at about 4 times the throughput rate possible with previously-known hydrofining catalysts such as cobalt-molybdenum. It appears quite obvious, therefore, that a marked increase in the capacity of a conventional hydrofining process should be achieved by the simple expedient of replacing some or all of the old hydrofining catalyst in use in the process with the more active nickel-molybdenum catalysts of high metal content. When this was done in a particular existing installation, however, it was surprisingly found that the ability of the process as a whole to purify the naphtha feed with respect to nitrogen removal was not increased to the expected extent. That is, it was expected that with the much more active catalyst it would be possible to increase the daily naphtha throughput to the hydrofining stage of a two-stage reforming process by a very substantial amount, while at the same time reducing the nitrogen content of the hydrofined naphtha to a lower concentration, such that increased throughput in the platinum reforming stage could also be accomplished. The following tabulation presents a comparison of previous operation using the cobalt-molybdenum catalyst to operation when ⅓ of the catalyst was replaced with four-fold more active nickel-molybdenum catalyst, in the particular installation.

	Previous Operation	New Operation	
		Expected	Observed
Average Temperature, ° F	775	750	750
Pressure, p.s.i.g	600	600	600
LHSV	2.4	3.0	2.4
S.c.f H_2/bbl	3,000	2,400	3,000
Product, p.p.m. N	0.3	0.2	0.4

As can be seen from the above data, the capacity of the hydrofining process could be only slightly increased, and the nitrogen content of the product could be only slightly improved, when the nickel-molybdenum catalyst was substituted for ⅓ of the cobalt-molybdenum catalyst. The further disappointing result was noted that, contrary to expectations, the on-stream time between catalyst regenerations was not greatly increased as compared to the

on-stream time between catalyst regenerations previously established with the cobalt-molybdenum catalyst.

It has now been found that certain special factors in combination were responsible for the poor showing in the above compared operation using the highly active catalyst in the particular installation, the significance of which factors was not previously recognized in the known process. It has now further been found how to modify the operation of the hydrofining process when such special factors prevail, so as to thereby obtain the desired improved results using the more active catalysts. The present invention relates to this new type of operation employed when such special factors prevail.

The factors referred to include the following, some of which take on greater significance in certain cases as compared to others:

(1) The naphtha feed employed in the test comparison above presented was of a more olefinic nature than usual, because the feed included a greater proportion of thermally and catalytically cracked naphthas as compared to straight run naphthas from distillation of crude petroleum. Because of the greater concentration of olefins, exothermic reactions including hydrogenation of olefins, occurring in the first catalyst bed contacted by the naphtha and hydrogen, increased the temperature by a very substantial amount.

(2) The end boiling point of the naphtha feed was slightly higher.

(3) The hydrogen was of slightly lower purity and available in lesser quantity, such that attempts to increase hydrogen purity in recycle gas by purging impurities lowered the total pressure.

(4) Although the nickel-molybdenum catalysts are more active than the cobalt-molybdenum catalysts at both high temperatures and at low temperatures, the difference between the relative activities is more pronounced at lower temperatures. Thus, the higher temperature operation did not obtain maximum advantage from the use of the nickel-molybdenum catalyst in terms of denitrification activity.

(5) Although the nickel-molybdenum catalysts are more resistant to fouling and deactivation than the cobalt-molybdenum catalysts at both high temperatures and at low temperatures, the differences in the relative rate of deactivation are more pronounced at lower temperatures. Thus, at the high temperature operation the maximum advantage of the nickel-molybdenum catalyst was not obtained in terms of rate of deactivation.

A major reason for the results in the test run being unsatisfactory is, therefore, considered to be that the temperature was too high. This is contrary to the established theories of hydrofining, because using higher temperatures has become standard practice for increasing nitrogen removal. Also, several factors dictate against the use of lower temperatures in the type of hydrofining process described, as follows:

(1) The activities of both the nickel-molybdenum and the cobalt-molybdenum hydrofining catalyst increase with increasing temperature. Thus, if it is necessary to use a very low temperature with the nickel-molybdenum catalyst, it becomes equally possible to obtain the same activity with a cobalt-molybdenum catalyst simply by using a much higher temperature. Because the nickel-molybdenum catalysts must inherently be somewhat more expensive than the cobalt-molybdenum catalysts, because of the greater amount of expensive metals employed per pound of catalysts, there is thus an incentive for continuing to use the less expensive, less active, catalyst at a higher temperature even though more frequently regeneration becomes necessary.

(2) Because of the presence of olefins, there will inherently be a large temperature rise accompanying their hydrogenation, thereby providing high temperature operation whether desired or not. If it is attempted to use a very low inlet temperature so that the temperature rise only results in a moderate operating temperature, it is found that all reactions are slowed down in the catalyst bed such that a greater quantity of catalyst would be needed, or else daily naphtha throughput could not be increased.

(3) The existing hydrofining processes applied to naphtha for preparation of catalytic reformer feed generally comprise passing recycle and makeup hydrogen and vaporized naphtha fed at elevated temperature at a pressure between 300 and 1000 p.s.i.g. substantially horizontally through stationary beds of catalyst particles contained in multiple serially-connected reactors. As was the case in the particular installation, wherein there are three reactors, these reactors are usually so constructed as to provide for radial flow of hydrogen and naphtha. That is, either the feed mixture enters the reactor in a central pipe, passes horizontally through a fixed-bed ring or "doughnut" of catalyst particles, and then collects in an annular space for discharge from the reactor, or the reverse flow is used. This construction permits high volumetric flow rates with low pressure drop. If this temperature is not maintained sufficiently high at the process pressure, i.e., above the dew point, some of the naphtha may condense, in which case the condensed portion would merely trickle as a stream along the bottom of the catalyst bed and contact only a minor portion of the catalyst. Any such liquid portion, which, even though small in volume, could contain a very large portion of the molecules in the feed, would be much less completely purified than the vaporized portion. This problem does not arise when naphtha and hydrogen are passed vertically downflow through a reactor containing a bed or beds of catalyst particles, because any portion of the naphtha which is condensed is evenly distributed across a cross-section of reactor, and it must trickle down through the beds, contacting just as much catalyst as the vaporized portion. Thus, the existing processes with radial-flow reactors have been designed for high tempearture vapor phase operation, and they have been operated with that in mind.

In accordance with the present invention, olefinic naphtha containing nitrogen compounds in concentrations deleterious to reforming catalyst is passed together with at least sufficient excess hydrogen to maintain the naphtha totally vaporized at 550° F. and the operating pressure, which is betwen 300 and 1000 p.s.i.g., into contact with a hydrofining catalyst at an inlet temperature above 550° F. The process of the invention applies to naphthas of such an olefinic nature that the temperature increases at least 75° F. above the inlet temperature to a temperature above about 700° F. during contacting with the catalyst due to exothermic reactions including hydrogenation of olefins. The excess hydrogen and partially hydrofined naphtha effluent of this contacting are then cooled by at least 50° F. to a temperature between 575° F. and 700° F. The cooled hydrogen and partially hydrogenated naphtha are then passed into contact with sufficient hydrofining catalyst of a type which is several times more active for hydrodenitrification than cobalt-molybdenum catalyst, at substantially the same pressure in the range 300–1000 p.s.i.g., to convert the deleterious nitrogen compounds contained therein substantially completely to ammonia. The resulting ammonia is then removed to recover catalytic reformer feed containing less than 1 p.p.m. nitrogen.

In an existing hydrofining process of the type wherein there are multiple serially-connected reactors for containing catalyst particles as stationary beds through which naphtha and hydrogen pass substantially horizontally, the invention provides a method of increasing the daily naphtha throughout withput without decreasing the on-stream time between catalyst regenerations, comprising replacing the catalyst particles in at least the reactors downstream of the first reactor with particles of catalyst which is at least three times more active for the conversion of nitrogen compounds at temperatures below 700° F. as compared

to cobalt-molybdenum hydrofining catalyst. The conventional cobalt-molybdenum catalyst can be retained in the first reactor. With the two different types of catalyst in the different reactors, it is thereafter necessary to modify the manner of conducting the process in several respects, in order to obtain the improved results of the invention. In particular, the dew point of the naphtha-hydrogen mixture must be maintained below the lowest temperature in any reactor, preferably below 550° F., at the hydrofining pressure employed, and the maximum hydrofining temperature in the reactors containing nickel-molybdenum catalyst must be maintained below about 700° F., preferably in the range between 600° F. and 700° F., at least during the initial and major portion of the on-stream time between catalyst regenerations.

To maintain the dew point of the naphtha-hydrogen mixture below the lowest temperature at the hydrofining pressure, a greater ratio of hydrogen to naphtha could theoretically be employed. Usually, however, in the existing process the ability to circulate hydrogen is limited by compressor capacity, and when the naphtha throughput is increased, the ratio of hydrogen to naphtha will necessarily decrease unless additional compression facilities are provided. Since it is desired, in accordance with the invention, to avoid adding such additional facilities, the dew point is instead controlled by monitoring the boiling range of the naphtha feed and adjusting it as necessary so that in the admixture with the available hydrogen the dew point will be below the lowest temperature in any reactor.

The dew point of the naphtha-hydrogen mixture can be lowered by using a lower pressure. It is found that although a lower hydrogen partial pressure decreases the rate of conversion of nitrogen compounds by about the same percentage with all catalysts, and increases the fouling or deactivation, the more active nickel-molybdenum catalysts are much less adversely affected with respect to fouling rate than conventional less active catalysts. Consequently, it is possible to increase naphtha throughput in an existing process even if a corresponding increased amount of hydrogen cannot be supplied or circulated.

It is not essential that the catalyst in the first reactor be the less active cobalt-molybdenum hydrofining catalyst, as the more active nickel-molybdenum catalyst could also be used in that reactor for the purpose of hydrogenating olefins. The activity for olefin hydrogenation is not as adversely affected, i.e ., not as rapidly lost as the activity for hydrogenating nitrogen compounds, by the higher temperatures employed in the first reactor. Hence the catalyst there could be any suitable catalyst for hydrogenation of olefins because the unusually high activity for hydrogenation of nitrogen compounds is not needed in the first reactor. Unless the naphtha throughput is to be nearly doubled, there is little incentive to use the more active catalyst in the first reactor except to eliminate having an inventory of two types of catalysts on hand. Also, it is advtantageous to use a less expensive, less active, catalyst in the first reactor because the catalyst there is exposed to contamination by trace impurities such as arsenic, or other metals which cannot be removed by regeneration, may also receive gross contamination by entrained heavy hydrocarbons, corrosion by-products and the like, and must bear the brunt of any upset in naphtha feed preparation.

The cooling of the hydrogen and partially hydrofined effluent of the first reactor prior to passing to the next reactor may be accomplished by indirect heat exchange with fresh feed or a portion thereof, for example, or with any other suitable cooling medium. In one embodiment, steam can be generated in the course of cooling the effluent of the first reactor. Alternately, cooling can be effected by adding to the effluent of the first reactor a small amount of cold fresh feed to accomplish rapid quenching. Preferentially, this would be a nonolefinic portion of the feed although this is not a necessary restriction if the amount of quench added is small in comparison to the total feed. As another possibility, cold recycle hydrogen-rich gas could be used as quench if hydrogen circulation facilities are adequate. Another possibility is to add cold liquid oil from the final recovery of catalytic reformer feed as quench.

In a preferred embodiment, the effluent is cooled by indirect heat transfer to the fresh feed. In the usual conventional existing hydrofining process the fresh feed is passed in series through at least two stages of heat exchange with the effluent of the final reactor in the chain of serially-connected reactors, and the partially preheated feed is then further preheated in a furnace. In the preferred embodiment of the invention the process is modified, without adding any new equipment, by heat exchanging the cold fresh feed in a first heat exchanger with the effluent of the last reactor in the train, and then further preheating the feed by heat exchange with a sufficient portion of the effluent of the first reactor in the train to thereby cool said effluent to the lower temperature of between 600° F. and 700° F. for entry into the next reactor. The feed is then further preheated by passing through the furnace as before.

The olefin content of the olefinic naphtha feed treated in the process is at least about 20% by volume. With greater than this amount of olefins in the feed the exothermic reactions including hydrogenation of said olefins will frequently cause the temperature to rise in the first bed of catalyst contacted by at least 75° F. and more usually by from 150 to 200° F. above the inlet temperature. It is desired that most of this olefin hydrogenation occurr in the first reactor, and accordingly the inlet temperature there is above 550° F., and more usually, above 650° F. Thus, the temperature achieved by the time the mixture of hydrogen and naphtha leaves the first catalyst chamber will be at least 725° F., and more usually in the neighborhood of 775° F. or higher. The maximum temperature rise depends of course not only upon the concentration of olefins but also on the ratio of hydrogen to naphtha feed. Ususally, this ratio is in the range between 2,000 and 15,000 standard cubic feed of hydrogen per barrel of naphtha, more usually between 2,000 and 6,000 s.c.f. per barrel.

The pressure used in all of the hydrofining reaction zones is usually rather close to the pressure used in the platinum reforming zone, though in some cases it is higher and in other cases it is lower. Where the platinum reforming is carried out at a low pressure close to 200 p.s.i.g., the hydrofining stage will usually be at a higher pressure because it is found necessary to use a pressure of at least 300 p.s.i.g. to obtain complete removal of nitrogen compounds. When the platinum reforming is carried out at a pressure in the neighborhood of 500 p.s.i.g., the hydrofining step will usually be carried out at that same pressure or at a somewhat lower pressure whereby hydrogen produced in the reforming process can be depressured directly to the hydrofining stage.

In the reaction zones wherein the more active hydrofining catalyst is used, the maximum temperature is to be maintained between 575° F. and 700° F. The most preferred conditions are in the lower end of this range, though usually the temperature at the inlet to the reactors containing the active catalyst will be between about 600 and 675° F . Thus, the cooling from the high temperature at the outlet of the first reactor to the low temperature at the inlet to the next reactor will be over a range of at least 50° F., and frequently the hydrogen and partially hydrofined naphtha will be cooled by 150° F. or more, sufficient to thereby maintain the maximum temperature in downstream reactors between 575 and 700° F. It must be remembered that the purifying reactions involving hydrogenation are also exothermic, and therefore there will be some further temperature increases in downstream reactors to take into consideration.

In the previous hydrofining processes it has not been unusual to use temperatures as high as 825° F. and even up to 850° F., though rarely are temperatures as high as 900° F. found to be operable. In the new process it will be found necessary to increase the operating temperatures in all of the catalyst beds as the catalyst deactivates or is fouled by the deposition of coke thereon. Nevertheless, it is found that, particularly in the case of the highly active nickel-molybdenum catalyst, the temperatures can and must be maintained in the range between 575 and 700° F. during at least the major and initial portion of the on-stream time between catalyst regeneration to obtain the maximum benefits of the invention. When it is necessary to use temperatures of above 725° F. in the reactors containing the more active catalyst, which should not occur until more than 60% of the desired run length has been attained, it will be found that the maximum increased naphtha throughput can no longer be sustained. When a temperature of above 775° F. is required, it will generally be found that the process cannot be operated at any greater naphtha throughput than when only the lower activity catalyst were used in all reactors. Further, there is little point in attempting to continue operation with the more active catalyst at temperatures above 800° F., unless it is essential to continue operation even at the expense of a reduced feed rate.

The following examples are presented to illustrate the practice of the invention and to show further the significance of various features therein, including the influence of olefins in the feed and the effect of processing conditions, particularly temperature, on the reaction rate and fouling rate using the more active catalyst as compared to previously known less active catalysts.

Example 1

A mixture of cracked and straight run naphthas, to be hydrorefined to prepare platformer feed containing no more than 0.3 p.p.m. nitrogen, has the following inspections:

Gravity, ° API	46.7
Aniline point, ° F.	78
Sulfur, wt. percent	0.9
Nitrogen, p.p.m.	263
Olefins, vol. percent	30
Aromatics, vol. percent	29
Boiling range, ° F.	205–417° F.

In the hydrofining process unit there are three identical, serially-connected, radial-flow reactors containing active cobalt-molybdenum-alumina hydrofining catalyst analyzing 3% Co and 8% Mo. The catalyst is sulfided as part of the startup procedure. At typical operating conditions early in the run, the naphtha and 4000 s.c.f. hydrogen-rich gas (80% H_2) per barrel of naphtha are preheated to about 550° F. at 800 p.s.i.g., by heat exchange with the effluent of the third reactor, and then to over 600° F. by passing through a fired furnace. Naphtha throughput is 2.4 liquid volumes per total volume of catalyst per hour. Reactor temperatures are as follows, to obtain product containing 0.3 p.p.m. nitrogen:

	Inlet (° F.)	Outlet (° F.)	Average (° F.)
1st reactor	608	734	671
2d reactor	734	750	742
3d reactor	750	760	755
Average			723

Four months later the catalyst has lost activity, and the inlet temperature has been increased to compensate, so that the average temperature is 800° F. The catalyst must be regenerated or the feed rate reduced, because the maximum heat output of the preheat furnace is being rapidly approached.

Example 2

The cobalt-molybdenum catalyst in the third (downstream) reactor of the unit described in Example 1 was replaced with 7% Ni–21% Mo-alumina catalyst known to be at least 3.5 times as active as fresh cobalt-molybdenum catalyst, the remaining Co–Mo catalysts being regenerated to fresh activity. The process was then operated with the feed, flow rate, pressure, and product nitrogen specification as in Example 1. Early in the run the temperature profile was as follows:

	Inlet (° F.)	Outlet (° F.)	Average (° F.)
1st reactor	577	704	641
2d reactor	704	720	712
3d reactor	720	730	725
Average			693

Four months later the temperature profile required for 0.3 p.p.m. nitrogen product was as follows:

	Inlet (° F.)	Outlet (° F.)	Average (° F.)
1st reactor	643	769	706
2d reactor	769	785	777
3d reactor	785	795	790
Average			758

The run can be continued about 50% longer than in Example 1, but not if it is attempted to increase the naphtha throughput significantly without the product nitrogen increasing.

Example 3

In accordance with the invention the cobalt-molybdenum catalyst in the second and third reactors is replaced with nickel-molybdenum-alumina catalyst analyzing 7% Ni and 21% Mo, the remaining cobalt-molybdenum catalyst in the first reactor being regenerated to to fresh activity, and all catalysts are sulfided. The piping is changed so that the feed is pre-heated by heat exchange with the effluent of the first reactor, then with the effluent of the third reactor, and then in the furnace. The naphtha throughput is increased to 3 LHSV, and the product nitrogen specification is lowered to 0.2 p.p.m. Ni. Early in the run this increased throughput and lower product nitrogen can be obtained with the following temperatures:

	Inlet (° F.)	Outlet (° F.)	Average (° F.)
1st reactor	575	701	638
2d reactor	625	641	633
3d reactor	641	651	646
Average			637

The catalysts deactivate only slowly at the lower average temperatures compared to Example 1. Four months later the temperature profile can be as follows:

	Inlet (° F.)	Outlet (° F.)	Average (° F.)
1st reactor	589	715	652
2d reactor	639	655	647
3d reactor	655	665	660
Average			653

The run can be continued more than twice as long as Example 1, even with the higher throughput and lower product nitrogen specification.

Example 4

The more active catalyst is used in the 2nd and 3rd reactors as in Example 3, but there is no cooling provided between the first and second reactors, the inlet temperature to the first reactor being instead lowered to the minimum permitted temperature of 550° F. The average temperature is 670° F., and the product nitrogen content is well below the permitted amount. The product nitrogen content soon increases, however, so that after four months on stream the temperature profile is substantially as in Example 2 at four months.

Example 5

The more active catalyst is placed in the first reactor. This works out quite well if the feed is not very olefinic. If the feed contains over about 20% olefins, the temperature rise across the first reactor makes the average temperature therein so high that nearly all the required denitrification is accomplished therein early in the run. The catalysts deactivate rapidly, however, so that by about four months the operation becomes as in Example 1. The less active catalyst in the downstream reactors loses activity by being exposed to the process conditions without ever contributing much in the way of nitrogen removal.

In the foregoing examples the more active catalyst was a sulfided nickel-molybdenum-alumina catalyst of high nickel and molybdenum content. It now being known that the making of catalysts several-fold more active than cobalt-molybdenum hydrofining catalysts is not an impossibility, and in view of the increasing interest in nitrogen removal, it is to be expected that other highly active catalysts of different composition may be found or may already be in existence. It is believed that catalysts containing as little as 3 weight percent Group VIII metal and as little as 13 weight percent Group VI metal, if carefully prepared, or using special supports, may be sufficiently more active (i.e., three times) than colbalt-molybdenum to be used as the more active catalyst in this invention even though on the basis of cost they might not be selected for use as a replacement for cobalt-molybdenum. Thus, the invention is not considered necessarily limited to the use of the exemplified catalysts. Rather the more active catalysts should be at least several-fold, and preferably at least three times, higher activity for denitrification than cobalt-molybdenum hydrofining catalyst, using as a standard the cobalt-molybdenum catalyst described in Example 1.

I claim:

1. A hydrofining process for preparing catalytic reformer feed containing less than 1 p.p.m. nitrogen from olefinic naphtha containing nitrogen compounds in concentration deleterious to platinum reforming catalysts, said naphtha containing at least 20% by volume olefins such that exothermic reactions including hydrogenation of olefins will cause a temperature rise greater than 75° F. when said naphtha and hydrogen are passed into contact with a hydrofining catalyst at reaction conditions including a temperature initially above 550° F. and a pressure between 300 and 1000 p.s.i.g., which process comprises the steps:

(1) passing a preheated mixture of said olefinic naphtha and at least sufficient excess hydrogen to maintain said naphtha totally vaporized at said reaction conditions into contact with a hydrofining catalyst at an inlet temperature sufficiently above 550° F. such that the temperature increases to above 700° F. during said contacting;

(2) cooling the mixture of hydrogen and partially hydrofined naphtha effluent of said contacting by at least 50° F. to a temperature between 575° F. and 700° F., said naphtha remaining totally vaporized;

(3) passing the cooled mixture of hydrogen and partially hydrofined naphtha into contact with a hydrofining catalyst of several-fold higher activity for denitrification than cobalt-molybdenum hydrofining catalyst, using as a standard the cobalt-molybdenum catalyst described in Example 1 of the foregoing specification, to convert deleterious nitrogen compounds remaining in said partially hydrofined naphtha substantially completely to ammonia, the cooling in step (2) above being to a temperature sufficiently below 700° F. such that the maximum temperature does not exceed 700° F. during contacting with the higher activity catalyst; and

(4) removing the ammonia resulting from the contacting of the above steps (1) and (3) from the effluent of the second-mentioned contacting.

2. The process of claim **1** wherein said hydrofining catalysts are contained in at least two serially-connected reactors as fixed beds of catalyst particles, through which beds hydrogen and vaporized naphtha pass substantially horizontally.

3. The process of claim **2** wherein the first reactor contains supported cobalt-molybdenum hydrofining catalyst and all reactors downstream of said first reactor contain supported nickel-molybdenum hydrofining catalyst of several-fold higher activity than said cobalt-molybdenum catalyst.

4. The process of claim **3** wherein said supported nickel-molybdenum hydrofining catalyst is composed essentially of nickel and molybdenum sulfides intimately associated with a predominantly alumina support, containing at least 4 weight percent nickel and at least about 19 weight percent molybdenum.

5. In a hydrofining process of the type wherein hydrogen and vaporized olefinic naphtha feed are passed at elevated temperature and a pressure between 300 and 1000 p.s.i.g. substantially horizontally through stationary beds of hydrofining catalyst particles contained in multiple serially-connected reactors without condensation of naphtha between reactors, in which process it is desired to convert to ammonia nitrogen compounds contained in said naphtha in excess of a specified maximum nitrogen content for catalytic reformer feed and consequently attempts to increase daily naphtha throughput necessitate using high temperatures above 750° F. in order to convert nitrogen compounds more rapidly, which high temperatures result in more rapid catalyst fouling creating a need for more frequent catalyst regeneration;

the method of increasing daily naphtha throughput without decreasing the on-stream time between catalyst regenerations, which method consists essentially of replacing hydrofining catalyst particles in at least one reactor down-stream of the first reactor with particles of supported hydrofining catalyst which is at least three times as active for the conversion of nitrogen compounds at temperatures below 700° F. as compared to cobalt-molybdenum hydrofining catalyst, increasing daily olefinic naphtha throughput, monitoring the boiling range of naphtha feed and adjusting as necessary to maintain the naphtha-hydrogen dew point below 550° F. at the hydrofining pressure, maintaining the inlet temperature to the first reactor above 550° F. whereby a temperature rise of at least 100° F. to a temperature above 700° F. occurs therein due to hydrogenation of olefins, and cooling the effluent of a preceding reactor prior to its entry into the next reactor sufficient to maintain the maximum hydrofining temperature in each reactor which contains the more active catalyst downstream of the first reactor between 600° F. and

700° F. during at least the initial and major portion of the on-stream time between catalyst regenerations.

6. The method of claim 5 wherein there are three serially-connected reactors, the hydrofining catalyst particles in the second and third reactors with respect to process flow are replaced with nickel-molybdenum-alumina catalyst containing between 4 and 10 weight percent nickel and between about 19 and 30 weight percent molybdenum, and the catalysts in all reactors are sulfided prior to thereafter conducting the process in the modified manner.

References Cited by the Examiner

UNITED STATES PATENTS

2,937,134	5/1960	Bowles	208—254
3,003,953	10/1961	Evans	208—254
3,071,542	1/1963	Davis et al.	208—254
3,228,993	1/1966	Kozlowski et al.	208—210

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