

METHOD FOR UPGRADING OF DIESEL FEED BY TREATMENT WITH SULFURIC ACID

FIELD OF THE INVENTION

[0001] The instant invention relates to a method for upgrading nitrogen-containing hydrocarbon streams. More particularly, the present invention relates to a method for producing low-sulfur, low-nitrogen diesel boiling range products involving contacting a diesel boiling range feedstream with an acidic solution to selectively remove heterocyclic nitrogen-containing compounds before hydrotreating.

BACKGROUND OF THE INVENTION

[0002] Currently, there exists a need to reduce the sulfur and aromatics content of motor fuels, in particular diesel, to meet current environmental emission regulations. While both the sulfur and aromatics content of diesel boiling range feedstreams from which diesel motor fuels are derived can be reduced to a satisfactory level through the use of catalytic treatments, the catalytic treatments are severely impeded by nitrogen-containing compounds present in the feedstream. Thus, many methods for reducing the nitrogen content in feedstreams, such as those used in sulfur and aromatics reducing processes, for motor fuel production have been proposed.

[0003] For example, United States Patent Number 3,719,587 teaches the use of dilute sulfuric acid (0-10 wt%) to remove basic nitrogen species from coal liquefaction derived naphtha. Unfortunately, hydrotreating catalysts are not only poisoned by basic nitrogen species, but also by non-basic nitrogen heterocycles that are abundant in diesel boiling range feedstreams. For this reason, stronger sulfuric acid has been used to remove substantially all of the nitrogen species.

-2-

[0004] Also, United States Statutory Invention Registration H1368, Fraytet, teaches the use of concentrated sulfuric acid, i.e. at least 95 wt.% sulfuric acid, to treat straight run jet fuel boiling range streams. The process requires that the sulfuric acid-containing stream be dispersed in the jet fuel in the form of droplets smaller than about 300 microns. The Fraytet process discloses that 90% or more of the nitrogen can be removed from the jet fuel boiling range stream. However, as Fraytet points out, separation of the acid from the feedstream is critical to avoid unwanted secondary reactions from occurring, such as, for example, polymerization of olefins and reaction of sulfuric acid with thiophenic species. These unwanted reactions are detrimental in several ways. First the unwanted side reactions force the practitioner of these processes to utilize more sulfuric acid because these reactions consume a portion of the sulfuric acid. Secondly, it degrades the product by forming high-boiling polymers from olefinic materials, which become soot-formers in subsequent combustion. Finally, some of the byproducts from these unwanted reactions are removed due to solubility in the acid byproduct and lead to an overall yield loss for the process.

[0005] However, it is also known in the art that dispersive contacting methods such as those of Fraytet have certain drawbacks such as "pepper sludge" formation. Pepper sludge formation occurs when the tiny droplets of acid are not readily coalesced or settled in gravity settlers. The dispersed acidic material suspended in the feed is thus carried over with the treated feed, and practitioners of such processes are forced to utilize caustic treatments to neutralize the pepper sludge and avoid corrosion problems. However, the "pepper sludge" suspended in the feed also contains nitrogen species that were removed from the feed. Upon neutralization, the nitrogen species are liberated

and return to the feed. Thus, the existence of pepper sludge in dispersive treatment methods limits the ultimate level of nitrogen reduction that can be achieved. Therefore, there exists a need in the art for a more effective nitrogen removal method for diesel boiling range feedstreams.

[0006] Therefore, there still exists a need in the art for a more effective nitrogen removal method for diesel boiling range feedstreams which benefits the hydroprocessing of the diesel boiling range feedstreams, i.e. a process that more selectively removes nitrogen-containing heterocycles that poison hydroprocessing catalysts without incurring the debits listed above that are the result of unwanted chemistry.

SUMMARY OF THE INVENTION

[0007] The instant invention is directed at an improved method for hydrotreating a diesel boiling range feedstream containing both nitrogen and sulfur contaminants and having a total acid number. The method comprises:

- a) providing a sulfuric acid solution having a sulfuric acid concentration of at least about 75 wt.%, based on the sulfuric acid solution;
- b) contacting a diesel boiling range feedstream containing both nitrogen and sulfur heteroatoms with the sulfuric acid solution under conditions effective at removing at least about 85 wt.% of the nitrogen compounds contained in said diesel boiling range feedstream thereby producing at least a diesel boiling range product and a used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the diesel boiling range feedstream; and
- c) hydrotreating said diesel boiling range product.

[0008] In one embodiment of the instant invention the sulfuric acid solution is a spent sulfuric acid solution obtained from an alkylation process unit wherein the spent sulfuric acid solution is produced by:

- a) combining an olefinic hydrocarbon feedstream containing C₄ olefins with isobutane to form a hydrocarbonaceous mixture; and
- b) contacting the hydrocarbonaceous mixture with sulfuric acid under conditions effective for producing at least an alkylate and a sulfuric acid solution having an acid concentration of at least about 75 wt.%.

[0009] Another embodiment of the instant invention is directed at an improved method for hydrotreating a diesel boiling range feedstream containing both nitrogen and sulfur contaminants and having a total acid number. The method comprises:

- a) providing a sulfuric acid solution having a sulfuric acid concentration of at least about 75 wt.%, based on the sulfuric acid solution;
- b) contacting a diesel boiling range feedstream containing both nitrogen and sulfur heteroatoms and having a total acid number with the sulfuric acid solution under conditions effective at removing at least about 85 wt.% of the nitrogen compounds contained in said diesel boiling range feedstream thereby producing at least a diesel boiling range product having a total acid number and a used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the diesel boiling range feedstream;
- c) contacting said diesel boiling range product with an effective amount of an acid reducing material selected from caustic and water under conditions effective at reducing the total acid number of said diesel boiling range product; and

d) hydrotreating said diesel boiling range product.

[0010] In one preferred embodiment, the acid reducing material is water.

[0011] In another preferred embodiment of the instant invention, the contacting of the diesel boiling range product with water reduces the total acid number of the diesel boiling product to at least the total acid number of the diesel boiling range feedstream.

BRIEF DESCRIPTION OF THE FIGURES

[0012] Figure 1 contains data obtained for Example 2 at 1 vol.% treat rate at various acid concentrations.

[0013] Figure 2 contains data obtained at 4 vol.% treat rate at various acid concentrations.

[0014] Figure 3 illustrates the combined impact of acid strength and treatment volume on the total nitrogen content of the feed.

[0015] Figure 4 shows the combined impact of acid strength and treatment volume on the total sulfur content of the feed.

[0016] Figure 5 shows the impact of both nitrogen removal and sulfur removal on yield loss.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0017] The instant invention is a method for removing nitrogen from diesel boiling range feedstreams containing both nitrogen and sulfur contaminants. The present method involves contacting, preferably by a non-dispersive method, a diesel boiling range feedstream containing both nitrogen and sulfur contaminants with a sulfuric acid solution thus producing a diesel boiling range product. The contacting of the diesel boiling range feedstream with the sulfuric acid solution reduces the nitrogen content of the diesel boiling range product by at least 85 wt.%. The resulting diesel boiling range product is then hydrotreated. It should be noted that hydrotreating and hydrodesulfurization are used interchangeably herein, and the phrase "diesel boiling range feedstream" is meant to refer to a diesel boiling range feedstream containing both nitrogen and sulfur contaminants and possessing a Total Acid Number ("TAN"). TAN is a measurement of the acidic content of an oil and is determined experimentally by titration of the oil with an appropriate base, as described for example in ASTM method number D664.

[0018] Feedstreams suitable for treatment with the present method boil within the diesel range. The diesel boiling range includes streams boiling in the range of about 300°F to about 775°F, preferably about 350°F to about 750°F, more preferably about 400°F to about 700°F, most preferably about 450°F to about 650°F. These include diesel boiling range feedstreams that are not hydrotreated, are a blend of non-hydrotreated diesel boiling range feedstreams, previously hydrotreated diesel boiling range feedstreams, blends of hydrotreated diesel boiling range feedstreams, and blends of non-hydrotreated and hydrotreated diesel boiling range feedstreams.

-7-

[0019] The diesel boiling range feedstreams suitable for treatment with the present method also contain nitrogen. Typically, the nitrogen content of such streams is about 50 to about 1000 wppm nitrogen, preferably about 75 to about 800 wppm nitrogen, and more preferably about 100 to about 700 wppm nitrogen. The nitrogen appears as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles.

[0020] In practicing the instant invention, the above-defined feedstream is intimately contacted with a sulfuric acid solution. The sulfuric acid solution used herein contains at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 75 wt.%, more preferably about 75 wt.% to about 88 wt.%. The sulfuric acid solution may be obtained through any means known. It is preferred that the sulfuric acid solution be the spent acid from an alkylation process unit having a sulfuric acid concentration within the above-defined ranges. A typical alkylation process involves combining an olefinic hydrocarbon feedstream containing C₄ olefins with isobutane to produce a hydrocarbonaceous mixture. This hydrocarbonaceous mixture is subsequently contacted with sulfuric acid. The sulfuric acid used for contacting the hydrocarbonaceous mixture is typically reagent grade sulfuric acid having an acid concentration of at least about 95 wt.%. Preferably the sulfuric acid has a sulfuric acid concentration of greater than about 97 wt.%. The hydrocarbonaceous mixture is contacted with the sulfuric acid under conditions effective at producing at least an alkylate and sulfuric acid solution. The sulfuric acid solution so produced comprises at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about

-8-

75 wt.%, more preferably about 75 wt. % to about 92 wt.%, about 0.5 to about 5 wt.% water, with the remaining balance being acid soluble hydrocarbons. It is more preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 82 and 92 wt.% sulfuric acid, about 1 to about 4 vol.% water, with the remaining balance being acid soluble hydrocarbons. However, it is most preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 85 and 92 wt.% sulfuric acid, about 1.5 to about 4 vol.% water, with the remaining balance being acid soluble hydrocarbons.

[0021] It should be noted that it is within the scope of the present invention to dilute the sulfuric acid obtained from the alkylation unit, or otherwise, with a suitable diluent, preferably water, in order to provide a sulfuric acid solution having the above-described concentration of sulfuric acid, i.e. at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 75 wt.%, more preferably about 75 wt.% to about 88 wt.%. In order to determine the sulfuric acid concentration once the diluent has been added to the sulfuric acid solution, the sulfuric acid content and water content are measured by standard analytical techniques. The equivalent acid strength can then be calculated with the following formula: $\text{equivalent wt\% sulfuric acid} = \frac{\text{wt\% sulfuric acid}}{(\text{wt\% sulfuric acid} + \text{wt\% water})}$. In this formula, the acid soluble hydrocarbon content of the spent alkylation acid is treated as an inert diluent with respect to the sulfuric acid and water content.

[0022] The diesel boiling range feedstream is contacted with the sulfuric acid solution at an acid volumetric treat rate of greater than about 0.5 vol.%, based on the diesel boiling range feedstream, preferably about 0.5 to about 20

vol.%, and more preferably 0.5 to about 5 vol.%. The contacting can be achieved by any suitable method including both dispersive and non-dispersive methods. Non-limiting examples of suitable dispersive methods include mixing valves, mixing tanks or vessels, and other similar devices. Non-limiting examples of non-dispersive methods include packed beds of inert particles and fiber film contactors such as those sold by Merichem Company and described in United States Patent Number 3,758,404, which is hereby incorporated by reference, which involve contacting along a bundle of metallic fibers rather than a packed bed of inert particles. Preferred contacting methods are non-dispersive, and more preferred contacting methods are those that are classified as dispersive.

[0023] The contacting of the diesel boiling range feedstream with the sulfuric acid solution occurs under effective conditions. By effective conditions, it is to be considered those conditions that allow the present method to achieve a reduction of nitrogen of greater than about 80 wt.%, preferably greater than about 85 wt.% more preferably greater than about 92 wt.%. Effective conditions are also to be considered those conditions that minimize yield losses during the sulfuric acid solution treatment to about to about 0.5 to about 6 wt.%, preferably about 0.5 to about 4 wt.%, more preferably about 0.5 to about 3 wt.%.

[0024] The contacting of the diesel boiling range feedstream with the sulfuric acid solution produces at least a diesel boiling range product that is sent to suitable aromatics and sulfur removal processes. Thus, the used sulfuric acid solution, which now contains the removed nitrogen species, must be separated from the diesel boiling range product. The used sulfuric acid

-10-

solution and the diesel boiling range product can be separated by any means known to be effective at separating an acid from a hydrocarbon stream. Non-limiting examples of suitable separation methods include gravity settling, electric field induced settling, centrifugation, microwave induced settling and settling enhanced with coalescing surfaces. However, it is preferred that the diesel boiling range product and the used sulfuric acid solution be separated, or allowed to separate, into layers in a separation device such as a settling tank or drum, coalescer, electrostatic precipitator, or other similar device. It is more preferred that the above-described fiber-film contactors be used for separating the used sulfuric acid solution and the diesel boiling range product produced by the present process. The diesel boiling range product can then be withdrawn from the separation device and passed to a suitable hydrotreating process.

[0025] The diesel boiling range product thus obtained by the present method will contain substantially less nitrogen, both basic and non-basic, than the initial diesel boiling range feedstream. By substantially less, it is meant that the nitrogen content of the diesel boiling range feedstream is reduced by at least about 80%, preferably at least about 85%, more preferably at least about 90%. Thus, it can likewise be said that the diesel boiling range product will have a nitrogen level about 80%, preferably at least about 85%, more preferably at least about 90% lower than that of the diesel boiling range feedstream. This will typically result in a diesel boiling range product having a nitrogen level of less than about 200 wppm, preferably less than about 100 wppm, more preferably less than about 50 wppm, and most preferably less than about 20 wppm. The contacting of the diesel boiling range feedstream with the sulfuric acid solution also typically results in a diesel boiling range product

-11-

having a TAN that is higher than the TAN of the diesel boiling range feedstream.

[0026] The diesel boiling range product will also typically have a sulfur concentration lower than that of the nitrogen-containing diesel boiling range feedstream. Thus, the contacting of the diesel boiling range feedstream with the sulfuric acid solution also reduces the sulfur content of the diesel boiling range product. The diesel boiling range product will therefore have a sulfur content lower than the diesel boiling range feedstream. However, it is desirable to minimize the reduction of sulfur to minimize yield losses. Typically the diesel boiling range product will have a sulfur content about 0.1 to about 25 % lower than the diesel boiling range feedstream, preferably about 0.1 to about 15% lower, more preferably about 0.1 to about 10% lower, and most preferably about 0.1 to about 5 % lower.

[0027] The diesel boiling range product is then hydrotreated to reduce sulfur levels. Any suitable hydrotreating catalyst can be used to hydrotreat the diesel boiling range product. Non-limiting examples of suitable hydrotreating catalysts are those that are comprised of at least one Group VIII metal oxide, preferably an oxide of a metal selected from Fe, Co and Ni, more preferably Co and/or Ni, and most preferably Co; and at least one Group VI metal oxide, preferably an oxide of a metal selected from Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. These catalysts can be arranged in any suitable manner such as, for example, fixed beds. It is also contemplated that more than one hydrotreating catalyst can be used, and more than one bed of catalysts can be used, e.g. a stacked bed configuration. The diesel boiling range product is contacted with the hydrotreating catalysts

-12-

under conditions effective at removing at least a portion of the sulfur contained in said diesel boiling range product. Preferably, that amount of sulfur necessary to meet current environmental regulatory standards is removed during the hydrotreating. As previously mentioned, the contacting of the diesel boiling range feedstream with the sulfuric acid solution typically results in a diesel boiling range product having a TAN that is greater than the TAN of the diesel boiling range feedstream. Thus, one embodiment of the instant invention involves contacting the diesel boiling range product, prior to hydrotreating, with an effective amount of a material selected from caustic and water, preferably water. By an effective amount of material, it is meant that amount of material that reduces the TAN of the diesel boiling range product. The diesel boiling range product is contacted with the caustic or water under effective conditions. By effective conditions, it is meant those conditions, that when selected, allow for the reduction of the TAN of the diesel boiling range product. Preferably the effective amount of material and the effective conditions are selected such that the TAN of the diesel boiling range product is equal that of the diesel boiling range feedstream. More preferably the effective amount of material and the effective conditions are selected such that the TAN of the diesel boiling range product is lower than that of the diesel boiling range feedstream.

[0028] The above description is directed to preferred embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0029] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

EXAMPLES

EXAMPLE 1

[0030] Two 10 ml samples of a virgin diesel, referred to herein as feed #1, were pipetted into two glass vials. One sample was combined with 0.1 ml (1 vol.% treat rate) of a reagent grade sulfuric acid solution having a sulfuric acid concentration of 96.1wt.%, and the other sample was mixed with the same sulfuric acid solution but with 0.2 ml (2 vol.% treat rate). The mixtures were shaken by hand for 60 seconds and then allowed to separate at room temperature. The two phases, i.e. the diesel boiling range product and the sulfuric acid solution, separated and the diesel product layers were removed. The diesel products were weighed and analyzed by ANTEK for nitrogen and sulfur contents. The results of this experiment are contained in Table 1 below.

EXAMPLE 2

[0031] A second diesel boiling range feedstream, referred to herein as feed #2, was also treated according to the method outlined in Example 1 above. The second diesel feedstream, however, contained about one-third cracked stock, i.e. light cat cycle oil and coker gas oil. A 2 liter sample of feed #2 was also treated in glass separatory funnels with the sulfuric acid solution described above in Example 1 at a 5vol.% treat rate. The results of these experiments are contained in Table 1 below.

TABLE 1					
Feed	Volumetric Treat Rate	wppm Nitrogen in Feed	wppm Nitrogen in Diesel Product	% Nitrogen Removal	Feed Recovered
#1	1 vol. %	107	5	95	98%
	2 vol. %	107	<2	98+	98%
#2	1 vol. %	392	158	60	96%
	2 vol. %	392	17	96	96%
	5 vol. %	392	3	99	96%

[0032] As can be seen in Table 1, both feeds responded well to treatment with the acidic solution, with nearly quantitative nitrogen removal. Low feed losses were also observed. The feed recovered was calculated by dividing the volume of diesel product recovered by the volume of the diesel feedstream and then multiplying by 100. It was also noted that the acidic solution by product from feed #2 became more fluid with increased acidic solution treat rates.

EXAMPLE 3

[0033] The experiments contained in Examples 1 and 2 above were repeated with spent sulfuric acid solution obtained from an alkylation unit. The composition of the spent alkylation acid was 90 wt% sulfuric acid, 4 wt% water and 6 wt% acid soluble hydrocarbon (by difference). The equivalent sulfuric acid concentration is 96wt.%. The results of these experiments are contained in Table 2 below.

TABLE 2				
Feed	Volumetric Treat Rate	wppm Nitrogen in Feed	wppm Nitrogen in Diesel Product	% Nitrogen Removal
#1	1 vol.%	107	4	96
	2 vol.%	107	1	99
#2	2 vol.%	392	18	95
	5 vol.%	392	3	99

[0034] As can be seen from Table 2, similar results are obtained by using the spent alkylation unit acid as are obtained using reagent grade sulfuric acid.

EXAMPLE 4

[0035] Twenty milliliters of a virgin diesel was equilibrated to 120°F in a water bath. The 20 ml sample was combined in a glass centrifuge tube with 0.2 ml (1 vol.% treat rate) of reagent grade sulfuric acid having an acid concentration of 96.1 wt.%. This mixture was shaken for 60 seconds and then subjected to ten minutes of centrifugation at 1500rpm. The diesel and the sulfuric acid solution separated rapidly, and the diesel layer was removed and analyzed by ANTEK for nitrogen and sulfur content.

[0036] This procedure was repeated at several acid concentrations. The acid concentration was reduced by adding distilled water to the reagent grade sulfuric acid.

[0037] The results of these experiments are contained in Figure 1, herein. As can be seen in Figure 1, the sulfur content of the feed is unaffected by the sulfuric acid treatment until the sulfuric acid solution reaches a sulfuric acid concentration of greater than about 80 wt.%. As the concentration of the acid increases from about 85 to about 94 wt.%, the sulfur loss increases and then levels off. In contrast, the nitrogen content of the diesel boiling range product

is reduced immediately by treatment with a sulfuric acid solution having an acid concentration of even 5 wt.% and continues to decrease with increases in acid strength until the sulfuric acid solution reaches a concentration of about 50 wt.%. The initial decrease in the total nitrogen concentration represents the removal of "basic" nitrogen species. However, the "non-basic" nitrogen species are unaffected by the sulfuric acid treatment until the concentration of sulfuric acid in the sulfuric acid solution reaches about 75 wt.%. At 75 wt.% acid strength, the sulfur species are unaffected.

[0038] Since one of the objects of the instant invention is to remove as much of the nitrogen as possible from the feed while minimizing yield losses, Figure 1 suggests that by using a sulfuric acid solution having an acid concentration within the range of about 75 wt.% to about 85 wt.%, this goal can be achieved. Though the data indicates that only 10% of the sulfur contained in the diesel boiling range feedstream is lost when using a sulfuric acid solution having an acid concentration of about 96 wt.%, this represents the largest single contributor to yield loss because the removal of sulfur removes the entire molecule in which the sulfur is contained.

EXAMPLE 5

[0039] Twenty milliliters of a diesel boiling range feedstream containing about one third cracked stock, i.e., light cat cycle oil and coker gas oil, was equilibrated to 120°F in a water bath. The 20 ml sample was combined in a glass centrifuge tube with 0.8 ml (4 vol.% treat rate) of reagent grade sulfuric acid having an acid concentration of 96.1 wt.%. This mixture was shaken for 60 seconds and then subjected to ten minutes of centrifugation at 1500rpm. The diesel and the sulfuric acid solution separated rapidly, and the diesel layer was removed and analyzed by ANTEK for nitrogen and sulfur content.

[0040] This procedure was repeated at several acid concentrations. The acid concentration was reduced by adding distilled water to the reagent grade sulfuric acid to dilute the acid concentration. Figure 2 contains the results of this experiment. As can be seen in Figure 2, treating the diesel containing cracked stock produced results similar to those that were described with respect to Figure 1.

[0041] Figure 3 includes results obtained through this experiment also. Figure 3 contains the nitrogen-reduction data obtained from treating the diesel boiling range feedstream containing cracked stock with various treat rates of sulfuric acid solutions having varied acid concentrations. As can be seen in Figure 3, nitrogen concentrations decrease with increased acid concentration.

[0042] Figure 4 includes results obtained through this experiment also. Figure 4 contains the sulfur-reduction data obtained from treating the diesel boiling range feedstream containing cracked stock with various treat rates of

sulfuric acid solutions having varied acid concentrations. As can be seen in Figure 4, sulfur concentrations decrease with increased acid concentration.

[0043] Figure 5 compares the nitrogen and sulfur removal data contained in Tables 3 and 4 with yield loss from treating the diesel boiling range feedstream containing cracked stock with various treat rates of sulfuric acid solutions having varied acid concentrations. Thus, Figure 5 illustrates the impact on yield loss from the removal of the nitrogen and sulfur species from the diesel feedstream. Thus, in viewing Figure 5, one can optimize a nitrogen removal method while minimizing feed loss.

EXAMPLE 6

[0044] 100 milliliters of virgin diesel having a total acid number ("TAN") of 0.26 mgKOH/g, a nitrogen concentration of 105 wppm, and a sulfur concentration 1.36 wt.% of was treated with sulfuric acid solution having a sulfuric acid concentration of 96 wt.%. The virgin diesel was treated by adding 1 ml of the sulfuric acid solution to the virgin diesel at room temperature, and shaking this mixture by hand in a separatory funnel for one minute. The mixture was then allowed to settle for 10 minutes and the spent acid solution and diesel boiling range product were decanted to recover the respective products.

[0045] The diesel boiling range product so recovered was separated into equal portions that were placed into 50 ml centrifuge tubes. The tubes were placed in a centrifuge operated at 1500 rpm for ten minutes. Acid sludge was observed at the bottom of the centrifuge tubes. One of the four samples was set

aside and marked "acid treated, centrifuged only", referred to herein as "Sample #1" for comparison with the other three samples.

[0046] 25 ml of diesel boiling range product from each respective centrifuge tube was pipetted into separate 50 ml centrifuge tubes for further treatment. To the first 25 ml sample, referred to herein as "Sample #2", 5 ml of distilled water was added. To the second and third samples, referred to herein as "Sample #3" and "Sample 4", respectively, was added 2.5 ml of a 5 wt.% NaOH solution. Samples 2, 3, and 4 were each shaken for 60 seconds, and then centrifuged for ten minutes at 1500 rpm. Sample #4 was then further treated by adding 5 ml of distilled water with subsequent shaking and centrifugation as defined above.

[0047] All of the Samples were submitted Galbraith Analytical Laboratories for TAN analysis. Sample 2 was observed to have a TAN of 0.37 mg KOH/g, illustrating that the sulfuric acid treatment increases the TAN of the diesel boiling range products. Sample #2 had a TAN of 0.25 mg KOH/g, illustrating that simple water washing was sufficient to lower the TAN to at least the level in the feedstream.

[0048] Sample #3 had a TAN below detection limits, which may be an erroneous reading due to caustic carryover. Sample #4 had a TAN of 0.03 mg KOH/g, essentially zero. It should be noted that water washing after caustic treating should minimize or eliminate caustic carryover, and that the nitrogen concentration of the diesel boiling range products was not reduced by the caustic and water washing.

-20-

[0049] Thus, Example #6 illustrates that simple water washing after sulfuric acid treatment is effective at lowering the TAN of the diesel boiling range product to at least that of the diesel boiling range feedstream, overcoming corrosion problems associated with typical acid treating processes.

CLAIMS:

1. An improved method for hydrotreating a diesel boiling range feedstream containing both nitrogen and sulfur contaminants comprising:
 - a) providing a sulfuric acid solution having a sulfuric acid concentration of at least about 75 wt.%, based on the sulfuric acid solution;
 - b) contacting a diesel boiling range feedstream containing both nitrogen and sulfur heteroatoms with the sulfuric acid solution under conditions effective at removing at least about 85 wt.% of the nitrogen compounds contained in said diesel boiling range feedstream thereby producing at least a diesel boiling range product and a used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the diesel boiling range feedstream; and
 - c) hydrotreating said diesel boiling range product.
2. The process according to claim 1 wherein the nitrogen-containing diesel boiling range feedstream boils in the range of about 300°F to about 775°F.
3. The process according to any preceding claim wherein the nitrogen-containing diesel boiling range feedstream boils in the range of about 400°F to about 700°F.
4. The process according to any preceding claim wherein the nitrogen-containing diesel boiling range feedstream contains about 50-1000 wppm nitrogen.

-22-

5. The process according to any preceding claim wherein the nitrogen present in said nitrogen-containing diesel boiling range feedstream includes carbazole and/or substituted carbazoles.
6. The process according to any preceding claim wherein said sulfuric acid solution contains greater than about 75 wt.% sulfuric acid.
7. The process according to any preceding claim wherein said sulfuric acid solution is obtained from an alkylation process unit.
8. The process according to any preceding claim wherein said alkylation process comprises:
 - a) combining an olefinic hydrocarbon feedstream containing C₄ olefins with isobutane to form a hydrocarbonaceous mixture; and
 - b) contacting the hydrocarbonaceous mixture with sulfuric acid under conditions effective for producing at least an alkylate and a sulfuric acid solution having an acid concentration of at least about 75 wt.%.
9. The process according to any preceding claim wherein water is added to said sulfuric acid solution to adjust the sulfuric acid concentration of said sulfuric acid solution.
10. The process according to any preceding claim wherein said diesel boiling range product has less than about 200 wppm nitrogen.

-23-

11. The process according to any preceding claim wherein the sulfur concentration of the diesel boiling range product is about 0.1 to about 25 wt.% less than the diesel boiling range feedstream.
12. The process according to any preceding claim wherein the yield loss attributed to the sulfuric acid solution treatment is about 0.5 to about 6 wt.%.
13. The process according to any preceding claim wherein the treat rate of the sulfuric acid solution is greater than about 0.5 vol.%.
14. The process according to any preceding claim wherein the treat rate of the sulfuric acid solution is about 0.5 to about 20 vol.%
15. The process according to any preceding claim wherein the nitrogen-containing diesel boiling range feedstream and the sulfuric acid solution are intimately contacted by a contacting method selected from non-dispersive and dispersive contacting methods.
16. The process according to any preceding claim wherein the non-dispersive contacting method is selected from packed inert particle beds and fiber film contactors.
17. The process according to any preceding claim wherein the dispersive contacting method is selected from mixing valves, static mixers and mixing tanks or vessels.

18. The process according to any preceding claim wherein said process further comprises separating said diesel boiling range product and said used sulfuric acid solution.
19. The process according to any preceding claim wherein the diesel boiling range product and the used sulfuric acid solution are separated by any means known to be effective at separating an acid from a hydrocarbon stream.
20. The process according to any preceding claim wherein the diesel boiling range product and the used sulfuric acid solution are separated by a separation device selected from settling tanks or drums, coalescers, electrostatic precipitators, and other similar devices.
21. The process according to any preceding claim wherein the diesel boiling range product and the used sulfuric acid solution are separated by fiber film contactors.
22. The method according to any preceding claim wherein the hydrotreating of the diesel boiling range product is achieved by contacting said diesel boiling range product with a hydrotreating catalysts containing at least one Group VI metal oxide and at least one Group VIII metal oxide under conditions effective at removing or converting at least a portion of the sulfur contained in said diesel boiling range product.
23. The method according to any preceding claim wherein said improved method further comprises contacting said diesel boiling range product with an effective amount of an acid reducing material selected from caustic and water

-25-

under conditions effective at reducing the total acid number of said diesel boiling range product prior to hydrotreating.

24. An improved method for hydrotreating a diesel boiling range feedstream containing both nitrogen and sulfur contaminants comprising:

- a) providing a sulfuric acid solution having a sulfuric acid concentration of greater than about 75 wt.%, based on the sulfuric acid solution;
- b) contacting a diesel boiling range feedstream containing both nitrogen and sulfur contaminants and boiling in the range of about 350°F to about 750°F with the sulfuric acid solution under conditions effective at removing greater than about 85 wt.% of the nitrogen compounds contained in said diesel boiling range feedstream thereby producing at least a diesel boiling range product and a used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the diesel boiling range feedstream and said contacting is achieved through the use of a non-dispersive method; and
- c) hydrotreating said diesel boiling range product by contacting said diesel boiling range product with a hydrotreating catalysts containing at least one Group VI metal oxide and at least one Group VIII metal oxide under conditions effective at removing or converting at least a portion of the sulfur contained in said diesel boiling range product.