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(54) Title: SUPERIOR EXTRACTION PERFORMANCE USING SULFURIC ACID

(57) **Abrégé/Abstract:**

The instant invention relates to a method for producing low-sulfur, low-nitrogen distillate boiling range products involving contacting a distillate boiling range feedstream with an acidic solution to selectively remove heterocyclic nitrogen-containing compounds before hydrotreating.

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SUPERIOR EXTRACTION PERFORMANCE USING 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 distillate boiling range products involving contacting a distillate 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 liquifaction 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.

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[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 may be

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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 distillate boiling range feedstreams which benefits the hydroprocessing of the distillate 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 hydrotreating process for distillate boiling range feedstream containing both nitrogen and sulfur contaminants and having a total acid number. The process 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 distillate boiling range feedstream containing both nitrogen and sulfur heteroatoms with the sulfuric acid solution under conditions effective at removing at least about 80 wt.% of the nitrogen compounds contained in said distillate boiling range feedstream thereby producing at least an effluent comprising at least a distillate boiling range product stream 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 distillate boiling range feedstream; and
- c) hydrotreating said effluent.

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[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 hydrotreating process for a distillate boiling range feedstream containing both nitrogen and sulfur contaminants and having a total acid number. The process 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 distillate 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 distillate boiling range feedstream thereby producing at least an effluent comprising at least a distillate boiling range product stream 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 distillate boiling range feedstream;
- c) separating said used sulfuric acid solution and said distillate boiling range product stream; and

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- d) contacting said distillate boiling range product stream 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 distillate boiling range product stream; and
- e) hydrotreating said distillate boiling range product stream.

[0010] In another embodiment of the instant invention, the distillate boiling range feedstream is a hydrotreated distillate boiling range feedstream.

[0011] In yet another embodiment of the instant invention, the distillate boiling range feedstream contains greater than 10 wt.% cracked stock, based on the distillate boiling range feedstream.

[0012] In one preferred embodiment, the acid reducing material is water.

[0013] In another preferred embodiment of the instant invention, the contacting of the distillate boiling range product stream with the acid reducing material reduces the total acid number of the diesel boiling effluent to at least the total acid number of the distillate boiling range feedstream.

BRIEF DESCRIPTION OF THE FIGURES

[0014] Figure 1 is a graph depicting acid strength versus distillate product stream nitrogen and yield loss, and thus, illustrates the sulfuric acid concentration in the various sulfuric acid solutions used in Example 1, hereof.

[0015] Figure 2 is a graph plotting acid strength versus yield loss, and thus, illustrates the sulfuric acid concentration of the various sulfuric acid solutions used in Example 2, hereof.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0016] The instant invention is an improved hydrotreating process involving removing nitrogen from distillate boiling range feedstreams containing both nitrogen and sulfur contaminants. The present invention involves contacting a distillate boiling range feedstream having a total acid number and containing both nitrogen and sulfur contaminants with a sulfuric acid solution thus producing at least an effluent comprising at least a distillate boiling range product stream and a used sulfuric acid solution. The contacting of the distillate boiling range feedstream with the sulfuric acid solution reduces the nitrogen content of the distillate boiling range feedstream by at least 80 wt.%. The resulting effluent is then hydrotreated. It should be noted that "distillate boiling range feedstream" is meant to refer to a distillate boiling range feedstream containing both nitrogen and sulfur contaminants and possessing a Total Acid Number ("TAN").

[0017] Feedstreams suitable for treatment in the present invention boil within the distillate range. The distillate boiling range includes streams boiling in the range of about 300°F to about 775°F, preferably about 350°F to about

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750°F, more preferably about 400°F to about 700°F, most preferably about 450°F to about 650°F. These include distillate boiling range feedstreams that are not hydrotreated, are a blend of non-hydrotreated distillate boiling range feedstreams, previously hydrotreated distillate boiling range feedstreams, blends of hydrotreated distillate boiling range feedstreams, and blends of non-hydrotreated and hydrotreated distillate boiling range feedstreams. The distillate boiling range feedstreams suitable for use herein can also contain greater than 10%, based on the distillate boiling range feedstream, of cracked stock. It should be noted that a hydrotreated distillate boiling range feedstream is to be considered a feedstream that has been contacted with an effective hydrotreating catalyst under effective hydrotreating conditions prior to being contacted with a sulfuric acid solution.

[0018] The distillate boiling range feedstreams suitable for treatment with the present method typically contain both nitrogen and sulfur impurities, i.e. heteroatoms. The nitrogen content of such streams is can range as high as about 2500 wppm nitrogen, preferably about 50 to about 2500 wppm nitrogen, more preferably about 75 to about 1000 wppm nitrogen, and most preferably about 100 to about 750 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. The sulfur content of such streams is typically about 40 wppm to about 35000 wppm sulfur, preferably about 250 wppm to about 35000 wt.% sulfur.

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[0019] In practicing the instant invention, the above-defined distillate boiling range feedstream is intimately contacted with a sulfuric acid solution. The sulfuric acid solution used herein is suited for the composition of the distillate boiling range feedstream treated. However, typical acid solutions contain greater than about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, and more preferably about 85 to about 93 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 a spent sulfuric acid solution. The latter is sometimes referred to as "spent alkylation acid". The sulfuric acid solution so produced comprises at least about 75 wt.% sulfuric acid, based on the 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 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 produced comprises between about 82 and 95 wt.% sulfuric acid, about 3 to about 10 wt % water,

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with the remaining balance being 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 93 wt.% sulfuric acid, about 4 to about 8 wt.% water, with the remaining balance being soluble hydrocarbons.

[0020] As mentioned above, the concentration of sulfuric acid in the sulfuric acid solution is dependent on the type of stream treated. If the distillate stream is a non-hydrotreated distillate or a blend of non-hydrotreated distillates, the sulfuric acid solution preferably has an acid concentration of greater than about 76 wt.%, a water concentration of about 2 wt.% to about 12 wt.%, and a dissolved oil concentration of less than about 12 wt.%; more preferably an acid concentration of about 85wt.% to about 89 wt.%, a water concentration of about 6 wt.% to about 10 wt.%, and a dissolved oil concentration of about 5 wt.% to about 9 wt.%. If the distillate stream is a hydrotreated distillate, or a blend of hydrotreated distillates, each of which may or may not contain cracked stock, the sulfuric acid solution preferably has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than about 12 wt.%. More preferably the acid concentration will be about 88 wt.% to about 93 wt.%, a water concentration of about 4 wt.% to about 6 wt.%, and a dissolved oil concentration of about 5 wt.% to about 10 wt.%. If the distillate stream is a non-hydrotreated distillate or a blend of distillates, containing greater than 10% cracked stock, based on the distillate or blend, the sulfuric acid solution preferably has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than about 12 wt.%. More preferably the acid

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concentration will be about 84 wt.% to about 91 wt.%, a water concentration of about 5 wt.% to about 10 wt.%, and a dissolved oil concentration of about 5 wt.% to about 12 wt.%.

[0021] It should be noted that it is within the scope of the present invention to dilute the sulfuric acid solution 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. greater than about 75 wt.% sulfuric acid, etc. 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 distillate 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 distillate boiling range feedstream, preferably about 1 to about 10 vol.%, and more preferably 1 to about 6 vol.%. If the distillate boiling range feedstream contains greater than about 40 wt.% cracked stock, then the most preferred treat rates are about 2 vol.% to about 6 vol.%, based on the distillate boiling range feedstream.

[0023] The contacting of the distillate boiling range feedstream and the sulfuric acid solution can be achieved by any suitable method including both

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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.

[0024] The contacting of the distillate 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 reduce the nitrogen content of the distillate boiling range feedstream by greater than about 80 wt.%, preferably greater than about 85 wt.% more preferably greater than about 90 wt.%. Effective conditions are also to be considered those conditions that minimize yield losses during the sulfuric acid solution treatment to about 0.5 to about 6 wt.%, preferably about 0.5 to about 4 wt.%, and more preferably about 0.5 to about 3 wt.%.

[0025] The contacting of the distillate boiling range feedstream with the sulfuric acid solution produces an effluent comprising at least a distillate boiling range product stream and a used sulfuric acid solution. In one embodiment of the instant invention the effluent is hydrotreated. However, it is preferred that the used sulfuric acid solution, which now contains the removed nitrogen species, be separated from the distillate boiling range product stream. The used sulfuric acid solution and the distillate boiling range product stream

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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 distillate boiling range product stream 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. In one embodiment, the above-described fiber-film contactors can be used for separating the used sulfuric acid solution and the distillate boiling range product stream. The distillate boiling range product stream can then be withdrawn from the separation device and conducted to a suitable hydroprocessing process.

[0026] The distillate boiling range product stream thus obtained contains substantially less nitrogen, both basic and non-basic, than the distillate boiling range feedstream. By substantially less, it is meant that the nitrogen content of the distillate boiling range product stream is at least about 80%, preferably at least about 85%, more preferably at least about 90% less than the distillate boiling range feedstream. Thus, it can likewise be said that the nitrogen content of the distillate boiling range feedstream is reduced by at least about 80%, preferably at least about 85%, and more preferably at least about 90%.

[0027] The sulfuric acid treatment, however, also results in a distillate boiling range product stream that is typically more acidic than the distillate boiling range feedstream. The measure of acidity referenced herein is the total acid number ("TAN") of the feedstream or effluent. The TAN is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample,

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required to titrate a sample to a specified end point, as measured by ASTM method D-664. A more acidic distillate boiling range product stream can have a detrimental effect on processing equipment, etc. because of its corrosive nature. Thus, one embodiment of the instant invention involves contacting the distillate boiling range product stream, prior to hydrodesulfurization, 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 distillate boiling range product stream. The distillate boiling range product stream is contacted with the acid reducing material under effective conditions. By effective conditions, it is meant those conditions, that when selected, allow for the reduction of the TAN of the distillate boiling range product stream. Preferably the effective amount of acid reducing material and the effective conditions are selected such that the TAN of the distillate boiling range product stream is equal that of the distillate boiling range feedstream. More preferably the effective amount of the acid reducing material and the effective conditions are selected such that the TAN of the distillate boiling range product stream is lower than that of the distillate oil boiling range feedstream.

[0028] The distillate boiling range product stream will also typically have a sulfur concentration lower than that of the distillate boiling range feedstream. Thus, the contacting of the distillate boiling range feedstream with the sulfuric acid solution also reduces the sulfur content of the distillate boiling range product stream. However, it is desirable to minimize the reduction of sulfur to minimize yield losses. Typically the distillate boiling range product stream will have a sulfur content about 0.1 to about 25 % lower than the distillate boiling range feedstream, preferably about 0.1 to about 5% lower.

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[0029] The distillate boiling range product stream is then hydrotreated to reduce sulfur and/or aromatics 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 distillate boiling range product stream is contacted with the hydrotreating catalysts under conditions effective at removing at least a portion of the sulfur contained in said distillate boiling range product stream. Preferably, that amount of sulfur necessary to meet current environmental regulatory standards is removed during the hydrotreating.

[0030] The above description is directed to several 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.

[0031] 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**

[0032] This experiment involved separately mixing samples of two distillate boiling range feedstreams with sulfuric acid solutions of varying strengths. Weaker acids were prepared by diluting, with water, a fresh sulfuric acid solution containing 96 wt.% acid and 4 wt.% water. The first distillate, referred to herein as Feed #1, was comprised of 60% virgin distillate and 40% cracked stock. Feed #1 contained 742 wppm nitrogen, 1.75 wt.% sulfur, and had an API Gravity of 26.2. The second distillate, referred to herein as Feed #2, was 100% virgin distillate. Feed #2 contained 100 wppm nitrogen, 1.25 wt.% sulfur, and had an API Gravity of 32.3.

[0033] Feed #1 was treated at a volumetric treat rate of 4 vol.%, based on Feed #1, and Feed #2 was treated at a volumetric treat rate of 1 vol.%, based on Feed #2. Samples (50 ml) of each feed were mixed in 100 cc centrifuge tubes with the varying strength sulfuric acid solutions and shaken by hand for 60 seconds and then allowed to separate at room temperature. The two phases, i.e. the distillate boiling range product stream and the sulfuric acid solution, separated and the distillate product stream layer was removed. The distillate products were weighed and analyzed by ANTEK for nitrogen and sulfur contents. The results of this experiment are contained in Figure 1, herein. Figure 1 shows a plot of acid strength versus distillate product stream nitrogen, and thus, illustrates the sulfuric acid concentration in wt.% of the various sulfuric acid solutions used.

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[0034] The data contained in Example 1 illustrates that higher nitrogen removal and greater yield loss are achieved with sulfuric acid solutions having a higher concentration of sulfuric acid.

EXAMPLE 2

[0035] This Example involved analyzing yield loss in relation to the sulfuric acid concentration of sulfuric acid solutions having varying concentrations of sulfuric acid. This Example involved three separate groups of experiments. In one group of experiments, the sulfuric acid solution used was a fresh sulfuric acid solution, as described above, at room temperature, and in another group of experiments, the fresh sulfuric acid solution was heated to 125°F. The spent alkylation acid used was at room temperature when it was mixed with Feed # 4 (a virgin distillate.)

[0036] This example involved separately mixing 50 ml samples of the virgin distillate, as described in Example 1, with varying strengths of both fresh and spent alkylation sulfuric acid solutions. An acid treat rate of 1 volume percent was used. Weaker acids were again prepared by diluting, with water, the fresh sulfuric acid solution and the spent sulfuric acid solution obtained from the alkylation unit.

[0037] The results of this experiment are contained in Figure 2, herein. Figure 2 shows a plot of acid strength versus yield loss, and thus, illustrates the sulfuric acid concentration of the various sulfuric acid solutions used. The yield loss is measured as a function of the ratio of acid to acid and water, wherein the ratio is taken as a measure of the concentration of sulfuric acid in

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the sulfuric acid solution used. In the case of spent alkylation acid the balance of the material that is not acid or water is acid soluble oil.

[0038] The data in Figure 2 demonstrates that when using sulfuric acid solutions having a sulfuric acid concentration of greater than about 92 wt.%, the spent alkylation sulfuric acid solution provided superior yield loss characteristics. The data in Figure 2 also illustrates that as the concentration of the sulfuric acid solution increases, so does the yield loss. Thus, when considering sulfuric acid solutions, one must balance nitrogen removal ability and yield loss. Therefore, this graph demonstrates that at higher acid strengths sulfuric acid obtained from an alkylation unit provides superior nitrogen removal and yield loss characteristics when compared to fresh sulfuric acid.

EXAMPLE 3

[0039] Several experiments were conducted by subjecting different feeds to continuous sulfuric acid treatments. Feeds #3 and #4 were 100% virgin distillate, Feeds #5, 6, and 7 were blends of 60% hydrotreated virgin distillate and 40% cracked stock, and Feed #8 was a cat cycle oil. This example was carried out by subjecting these Feeds to continuous sulfuric acid treatment involving contacting the acid and the oil over a fiber film-type non-dispersive contactor and separating the contacted phases by gravity. In these experiments fresh sulfuric acid, containing only acid and water, was used. The experiments were performed at between 100° F and 125° F. The spent acid was recycled and recombined with fresh acid to achieve equilibrium or near equilibrium contacting between the acid and the oil. The acid-treated oil is separated from the spent acid and then contacted with caustic in a separate fiber film contactor and separated from the caustic by gravity settling. The treat rates, acid

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concentration nitrogen removal, yield loss, acid carryover, and the emulsion of sulfuric acid in the feed are contained in Table 1, below.

TABLE 1

Feed	Feed #3	Feed #4	Feed #5	Feed #6	Feed #7	Feed #8
Treat Rate, vol. %	1.2	1	2.0	1.4	1.4	4.0
Feed Acid wt % acid	96	91	96	96	91	91
Feed Acid wt % water	4	9	4	4	9	9
% N Removal	95%	87%	98%	97%	59%	86%
% Yield Loss	1.4%	0.6%	1.7%	1.3%	undetermined	3.3%
% Acid Carry Over	1.5%	5.8%	1.2%	0.5%	undetermined	<0.5%
Acid:Oil Emulsion	Small	Small	not measured	None	Large	None

[0040] Acid carry over is determined by measuring the amount of nitrogen that is returned to the oil during the caustic wash step (Nc) and comparing this value with the amount of nitrogen that was removed from the oil in the acid contacting step. (Na) Mathematically we have: % Carry Over = 100 x Nc/Na.

[0041] The ease of separation of the acid and oil phases is qualitatively measured by examining the size of the any acid:oil emulsion layer at the end of the gravity settler after the acid:oil contactor. The greater the size of the emulsion layer, the more difficult the separation.

[0042] Table 1 demonstrates that certain minimum fresh acid strengths are necessary to have a high degree of nitrogen removal from various feeds. Unexpectedly, with high strength acids it is possible to remove substantially all

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(>98%) of the nitrogen species through sulfuric acid extraction. This is true even of hydrocarbon streams containing cracked material.

[0043] The inventors hereof have also unexpectedly discovered that fresh acids with higher water concentration produce spent acids with lower viscosities, and cracked stock in the hydrocarbon feed contributes to higher viscosities in the spent acid. The inventors hereof have also unexpectedly discovered that the amount of water in the fresh acid contributes to the emulsion-forming characteristics of the spent acid, with greater amounts of water leading to greater emulsions, wherein this characteristic is also dependent on the hydrocarbon feed. Thus, the inventors hereof have discovered that there exist conditions of treat acid composition which allow low hydrocarbon yield loss, high nitrogen removal and produce a spent acid of low viscosity, which is less susceptible to emulsion when contacted with the treated oil.

EXAMPLE 4

[0044] To demonstrate the embodiment of the instant invention involving contacting the distillate boiling range product stream with an acid reducing material to reduce the Total Acid Number ("TAN") of the distillate boiling range product stream, 100 milliliters of virgin distillate having a total acid number ("TAN") of 0.26 mgKOH/g, a nitrogen concentration of 105 wppm, and a sulfur concentration of 1.26 wt.% was treated with a sulfuric acid solution having a sulfuric acid concentration 96 wt.%. The virgin distillate was treated by adding 1 ml of the sulfuric acid solution to the virgin distillate 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

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spent acid solution and distillate boiling range product were decanted to recover the respective products.

[0045] The distillate 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 distillate boiling range product from each respective centrifuge tube was pipetted into separate 50 ml centrifuge tubes for further treatment. To the first 25ml sample, referred to herein as "Sample #2", 5ml 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 5ml of distilled water with subsequent shaking and centrifugation as defined above.

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

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

[0049] Thus, Example #4 illustrates that simple water washing after sulfuric acid treatment is effective at lowering the TAN of the distillate boiling range product to at least that of the distillate boiling range feedstream, overcoming corrosion problems associated with typical acid treating processes.

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CLAIMS:

1. An improved method for hydrotreating a distillate boiling range feedstream containing both nitrogen and sulfur contaminants and having a total acid number 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 distillate boiling range feedstream containing both nitrogen and sulfur heteroatoms with the sulfuric acid solution under conditions effective at removing at least about 80 wt.% of the nitrogen compounds contained in said diesel boiling range feedstream thereby producing at least an effluent comprising at least a distillate boiling range product stream 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 distillate boiling range feedstream; and
 - c) hydrotreating said distillate boiling range product.
2. The process according to claim 1 wherein the distillate boiling range feedstream boils in the range of about 300 to about 775°F.
3. The process according to any preceding claim wherein the distillate 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 distillate boiling range feedstream contains about 25-2500 wppm nitrogen.

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5. The process according to any preceding claim wherein the nitrogen present in said distillate 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 80 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 a diluent 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 the sulfur concentration of the distillate boiling range product stream is about 0.1 to about 25 % wt.% less than the distillate boiling range feedstream.

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11. 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.%.
12. The process according to any preceding claim wherein the treat rate of the sulfuric acid solution is about 0.5 to about 20 vol.%
13. The process according to any preceding claim wherein the nitrogen-containing distillate boiling range feedstream and the sulfuric acid solution are intimately contacted by a contacting method selected from non-dispersive and dispersive contacting methods.
14. The process according to any preceding claim wherein the contacting method is selected from packed inert particle beds and fiber film contactors.
15. The process according to any preceding claim wherein the dispersive contacting method is selected from mixing valves, static mixers and mixing tanks or vessels.
16. The process according to any preceding claim wherein the distillate boiling range product stream and the used sulfuric acid solution are separated by any means known to be effective at separating an acid from a hydrocarbon stream.
17. The process according to any preceding claim wherein the distillate 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.

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18. The process according to any preceding claim wherein the distillate boiling range product and the used sulfuric acid solution are separated contacted by fiber film contactors.
19. The method according to any preceding claim wherein the hydrotreating of the effluent is achieved by contacting said effluent 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 distillate boiling range product.
20. The method according to any preceding claim wherein said improved method further comprises contacting said distillate boiling range product stream 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 distillate boiling range product prior to hydrotreating.
21. The process according to any preceding claim wherein the distillate stream is a non-hydrotreated distillate or a blend of non-hydrotreated distillates.
22. The process according to any preceding claim wherein the sulfuric acid solution has an acid concentration of greater than about 76 wt.%, a water concentration of about 2 wt.% to about 12 wt.%, and a dissolved oil concentration of less than about 12 wt.%.

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23. The process according to any preceding claim wherein the distillate stream is a hydrotreated distillate, or a blend of hydrotreated distillates, each of which may or may not contain cracked stock.

24. The process according to any preceding claim wherein the sulfuric acid solution has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than about 12 wt.%.

25. The process according to any preceding claim wherein the distillate stream is a non-hydrotreated distillate or a blend of hydrotreated distillates, containing greater than 10% cracked stock, based on the distillate or blend.

26. The process according to any preceding claim wherein the sulfuric acid solution has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than about 12 wt.%.

27. The method according to any preceding claim wherein the distillate boiling range feedstream contains greater than 40 wt.% cracked stock.

28. The process according to any preceding claim wherein the sulfuric acid solution treat rate is about 3 vol.% to about 6 vol.% based on the distillate boiling range feedstream.

29. An improved hydrotreating process for distillate boiling range feedstreams boiling in the range of about 300 to about 775°F and containing

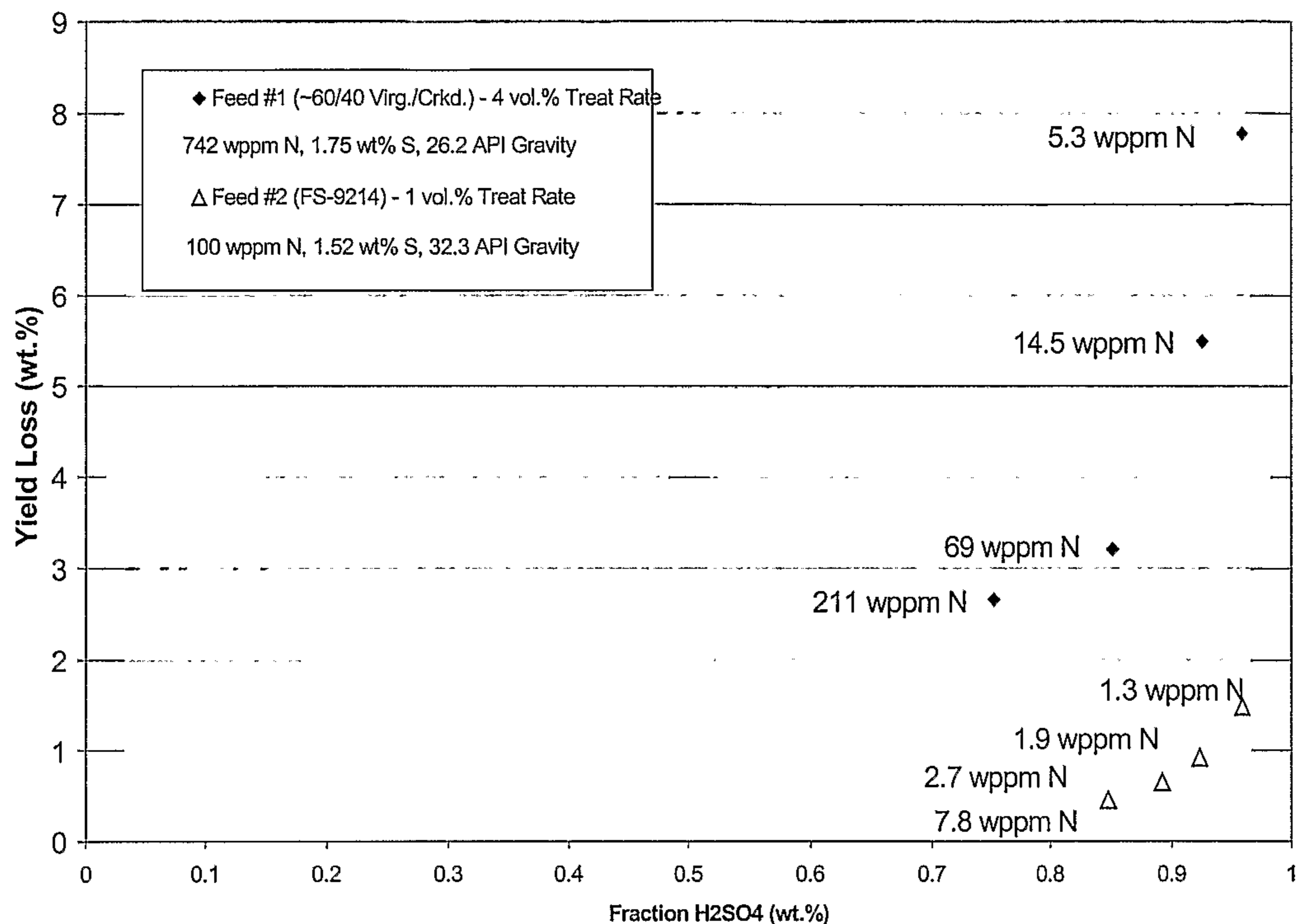
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about 50 to about 2500 wppm nitrogen and about 40 wppm to about 35000 wppm sulfur contaminants and having a total acid number comprising:

- 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 the distillate 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 distillate boiling range feedstream thereby producing at least an comprising at least a distillate boiling range product stream and a used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is about 1 to about 10 vol.% to about, based on the distillate boiling range feedstream;
- c) separating said used sulfuric acid solution and said distillate boiling range product stream; and
- d) contacting said distillate boiling range product stream 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 distillate boiling range product stream; and
- e) hydrotreating said distillate boiling range product stream by contacting said distillate boiling range product with a hydrotreating catalyst 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 distillate boiling range product stream.

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Figure 1



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Figure 2