

**METHOD FOR UPGRADING CATALYTIC CRACKING
FEEDS BY TREATMENT WITH A SULFURIC ACID SOLUTION**

FIELD OF THE INVENTION

[0001] The instant invention relates to an improved catalytic cracking method for hydrocarbon streams. More particularly, the present invention relates to the use of an acid treatment method to remove heterocyclic nitrogen-containing compounds from a feedstream and then subjecting the feedstream having a reduced amount of nitrogen-containing compounds to catalytic cracking.

BACKGROUND OF THE INVENTION

[0002] Currently, there exists a need to reduce the heterocyclic nitrogen content of feedstreams used in catalytic cracking operation because these heterocyclic nitrogen-containing compounds, especially basic heterocyclic nitrogen-containing compounds, act as competitive inhibitors on the acidic cracking sites of cracking catalysts. These nitrogen-containing compounds are indigenous to crude oils, and are typically concentrated in the higher boiling fractions such as virgin gas oils (VGOs). The presence of these heterocyclic nitrogen-containing compounds, even at levels as low as hundreds weight parts per million ("wppm"), significantly reduce catalytic conversions in catalytic cracking operations. Typically, catalytic cracking operations experience a 1% decrease in conversion for every 100 wppm of nitrogen in the feed to the process. Thus, many methods for reducing the nitrogen content in feedstreams, such as those used in catalytic cracking operations, have been proposed.

[0003] For example, 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

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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.

[0004] Therefore, there still exists a need in the art for a more effective nitrogen removal method for catalytic cracking boiling range feedstreams because the overall catalytic cracking operation would be improved.

SUMMARY OF THE INVENTION

[0005] The instant invention is directed at an improved catalytic cracking method involving removing nitrogen from a nitrogen-containing catalytic cracking boiling range feedstream. The method comprises:

- a) providing a sulfuric acid solution containing greater than about 75 wt.% sulfuric acid;
- b) contacting a nitrogen-containing catalytic cracking boiling range feedstream with the sulfuric acid solution in a first reaction stage under effective conditions and at an acid solution volumetric treat rate greater than about 0.5 vol.%, based on the catalytic cracking boiling range feedstream, wherein greater than about 60 wt.% of the nitrogen compounds contained in said catalytic cracking boiling range feedstream is removed thereby producing a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution; and
- c) conducting at least a portion of said first reaction stage effluent to a second reaction stage wherein said first reaction stage effluent is contacted under effective cracking conditions with a cracking catalyst.

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[0006] 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
- a) 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.%.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0007] It should be noted that "cat cracker" and "catalytic cracking" are used interchangeably herein. These terms are meant to encompass all catalytic cracking operations such as, for example, fluidized catalytic cracking, steam cracking, hydrocracking, etc.

[0008] The instant invention is an improved catalytic cracking method involving removing nitrogen compounds from nitrogen-containing catalytic cracking boiling range feedstreams. The present method involves contacting a catalytic cracking boiling range feedstream in a first reaction stage with a sulfuric acid solution to reduce the nitrogen content of the catalytic cracking boiling range feedstream by at least about 60 wt.%. The contacting of the catalytic cracking boiling range feedstream with the sulfuric acid solution produces a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution. At least a portion of the first reaction stage effluent is then conducted to a second reaction stage

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wherein the first reaction stage effluent is contacted under effective conditions with a cracking catalyst.

[0009] Feedstreams suitable for treatment with the present nitrogen reduction method include any conventional catalytic cracking operation feedstreams. Such feedstreams typically include heavy hydrocarbonaceous feeds boiling in the range of about 430°F to about 1050°F (220-565°C), such as gas oils, heavy hydrocarbon oils comprising materials boiling above 1050°F (565°C); heavy and reduced petroleum crude oil; petroleum atmospheric distillation bottoms; petroleum vacuum distillation bottoms; pitch, asphalt, bitumen, other heavy hydrocarbon residues; tar sand oils; shale oil; liquid products derived from coal liquefaction processes; and mixtures thereof. The cat cracker feedstream may also comprise recycled hydrocarbons, such as light or heavy cycle oils. Preferred feeds for use in the presently disclosed method are vacuum gas oils boiling in the range above about 650°F (343°C).

[0010] The catalytic cracking boiling range feedstreams suitable for treatment with the present method also contain heterocyclic nitrogen-containing compounds. Typically, the nitrogen content of such streams is about 10,000-100 wppm preferably about 5000-200 wppm, and more preferably about 3000-500 wppm. The nitrogen compounds appears as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species include quinolines and substituted quinolines, benzo quinolines such as acridine, anilines, N-alkyl indoles, alkylarylamines and substituted derivatives thereof. Non-limiting examples of non-basic nitrogen species include indoles,

carbazoles, benzocarbazoles, amides such as quinolone and substituted derivatives thereof.

[0011] Catalytic cracking boiling range feedstreams suitable for treatment with the present method also contain metals such as nickel, vanadium, copper, iron, and sodium. The total metals concentration in the cat cracker boiling range feedstreams is typically from about 10 to about 1000 wppm, preferably about 50 to about 500 wppm, more preferably from about 100 wppm to about 300 wppm.

[0012] In practicing the instant invention, the above-defined catalytic cracking boiling range feedstreams are intimately contacted with a sulfuric acid solution in a first reaction stage to remove at least 60 wt.% of the nitrogen species, both basic and non-basic, thus producing a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution. Sulfuric acid solutions suitable for use herein contain at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, more preferably greater than about 85 wt.%, most preferably from about 85 wt.% to about 93 wt.%. The sulfuric acid solution may be obtained through any means known.

[0013] It is preferred that the sulfuric acid solution be a spent sulfuric acid solution obtained from an alkylation process unit and have 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

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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 sulfuric acid solution. The sulfuric acid solution so produced comprises at least about 75 wt.% sulfuric acid, 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 93 wt.% sulfuric acid, about 1 to about 4 wt.% 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 93 wt.% sulfuric acid, about 1.5 to about 4 wt.% water, with the remaining balance being acid soluble hydrocarbons.

[0014] It should be noted that it is within the scope of the present invention to dilute the sulfuric acid solutions 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 greater than about 85 wt.%, most preferably from about 85 wt.% to about 93 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

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by standard analytical techniques. The equivalent acid strength can then be calculated with the following formula: $\text{equivalent wt.\% sulfuric acid} = \frac{\text{wt.\% sulfuric acid}}{(\text{wt.\% sulfuric acid} + \text{wt.\% water})}$. For example, if a spent alkylation acid contains 87 wt.% sulfuric acid, 6 wt.% water and 7 wt.% acid soluble hydrocarbons, the equivalent sulfuric acid concentration of this acid is 94 wt. ($87/(87+6)$). Thus, one can add water to this spent alkylation acid to adjust its equivalent strength to a concentration range discussed above.

[0015] The catalytic cracking boiling range feedstream is contacted with the sulfuric acid solution under effective conditions and at an acid volumetric treat rate of greater than about 0.50 vol.%, based on the catalytic cracking boiling range feedstream, preferably about 0.5 to about 20 vol.%, more preferably about 0.5 to about 10 vol.%, and most preferably 0.50 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, propeller mixers, in-line static mixers, and orifice plates. 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. In one embodiment, the contacting methods are non-dispersive, and in another embodiment, the contacting methods are those that are classified as dispersive.

[0016] As stated above, the contacting of the cat cracker 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 in the catalytic cracking boiling range feedstream of greater than about 60 wt.%, preferably greater than about 75 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 30 wt.%, preferably about 0.5 to about 20 wt.%, more preferably about 0.5 to about 10 wt.%.

[0017] The contacting of the catalytic cracking boiling range feedstream with the sulfuric acid solution in the first reaction stage produces a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution. At least a portion, preferably substantially all, of the first reaction stage effluent is thence conducted to a second reaction stage wherein it is contacted, under effective cracking conditions, with a cracking catalyst. However it is preferred to separate the first reaction stage effluent into at least a catalytic cracking boiling range effluent and a used sulfuric acid solution, which now contains the removed nitrogen species. The used sulfuric acid solution and catalytic cracking boiling range effluent 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 catalytic cracking boiling

range effluent 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 also possible to use the above-described fiber-film contactors for separating the used sulfuric acid solution and the catalytic cracking boiling range effluent produced by the present method. At least a portion, preferably substantially all, of the catalytic cracking boiling range effluent can then be conducted to a suitable cracking operation.

[0018] As stated above, effective conditions for contacting the catalytic cracking boiling range feedstream with the sulfuric acid solution are also to be considered those conditions that minimize yield losses to the used sulfuric acid solution. Thus, the catalytic cracking boiling range effluent is typically greater than about 70 wt.% of the cat cracker feedstream, preferably greater than about 80 wt.%, more preferably greater than about 90 wt.%, with the remainder being contained in the used sulfuric acid solution separated from the catalytic cracking boiling range effluent. While not wanting to be limited by theory, the inventors hereof attribute the loss in yield to compounds such as coke precursors, 4-ring aromatics, and polar compounds. It should be noted that the amount of catalytic cracking boiling range effluent contained in the separated used sulfuric acid solution can also be recovered and combined with the catalytic cracking boiling range feedstream as a recycle stream, if desired.

[0019] The catalytic cracking boiling range effluent will typically contain less nitrogen, both basic and non-basic, than the initial catalytic cracking boiling range feedstream. The nitrogen content of the catalytic cracking

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boiling range feedstream is reduced by greater than about 60 wt.%, preferably greater than about 75 wt.%, more preferably greater than about 90 wt.%. Thus, catalytic cracking boiling range effluent will contain 60 wt.%, etc. less nitrogen than the catalytic cracking boiling range feedstream.

[0020] The catalytic cracking boiling range effluent will also typically have a lower total metals concentration, such as the sum of, for example, Ni, V, Fe, Cu, Na metals, than the initial catalytic cracking boiling range feedstream. The total metals concentration in the catalytic cracking boiling range product typically ranges from about 20 wppm to about 1000 wppm, preferably from about 10 wppm to about 500 wppm, more preferably from about 5 wppm to about 30 wppm.

[0021] At least a portion of the first reaction stage effluent, or catalytic cracking boiling range effluent in preferred embodiments, is sent to a suitable catalytic cracking operation. Non-limiting examples of suitable catalytic cracking operations include fluidized catalytic cracking and hydrocracking. In the catalytic cracking operation employed, any suitable cracking catalyst can be employed to obtain the desired product. The conditions under which the first reaction stage effluent is contacted with the cracking catalyst are not critical to the instant invention and can be any conditions effective at producing the desired products, i.e. naphtha, diesel, etc. Thus, in practicing the present invention, the practitioner selects a cracking catalyst or catalysts, and then selects conditions that are effective for use with that particular catalyst or catalysts. For example, if the catalytic cracking boiling range product is passed to a fluidized catalytic cracking ("FCCU") reactor, any FCCU catalyst can be

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used, and the FCCU reactor would be operated under effective conditions for that particular catalyst. Likewise, if the catalytic cracking boiling range product is passed to a hydrocracking reactor, a suitable hydrocracking catalyst such as, for example a zeolite, can be selected and the hydrocracking reactor conditions such as, for example, hydrogen treat rate, liquid hourly space velocity, etc. would be selected from conditions known to be effective with that particular catalyst or catalysts.

[0022] It should be noted that the present nitrogen reduction method also benefit downstream catalytic processes such as desulfurization processes that are utilized on some products, such as naphtha and diesel boiling range products, that are produced by catalytic cracking operations. It should also be noted that the catalytic cracking boiling range effluent will also typically have a sulfur concentration lower than that of the nitrogen-containing catalytic cracking boiling range feedstream. Thus, the contacting of the catalytic cracking boiling range feedstream with the sulfuric acid solution also reduces the sulfur content of the catalytic cracking boiling range effluent. The catalytic cracking boiling range effluent will therefore have a sulfur content lower than the catalytic cracking boiling range feedstream. However, it is desirable to minimize the reduction of sulfur to minimize yield losses. Typically the catalytic cracking boiling range effluent will have a sulfur content about 0.1 to about 25 % lower than the catalytic cracking boiling range feedstream, preferably about 0.1 to about 15% lower, more preferably about 0.1 to about 10% lower, and most preferably about preferably about 0.1 to about 5 % lower.

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[0023] 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.

[0024] 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

[0025] Three 20 ml samples of virgin gas oil were diluted with 5ml of toluene to reduce the viscosity at room temperature, and combined with a sulfuric acid solution in a glass centrifuge tube. One sample was combined with 0.4 ml (2 vol.% treat rate) of a reagent grade sulfuric acid solution, referred to herein as solution #1, having a sulfuric acid concentration of 96 wt.%. The other two samples were mixed with the same sulfuric acid solution but with 0.8 ml (4 vol.% treat rate) and 20 ml (10 vol.% treat rate), respectively. The mixtures were shaken by hand for 60 seconds and then allowed to separate at room temperature. The two phases, i.e. the cat cracker boiling range product and the sulfuric acid solution, separated and the cat cracker product layer was removed. The cat cracker product thus removed was stripped of toluene under vacuum, weighed and analyzed by ANTEK for nitrogen content. The results of this experiment are contained in Table 1 below.

TABLE 1					
Feed	Volumetric Treat Rate	wppm Nitrogen in Feed	wppm Nitrogen in Product	% Nitrogen Removal	Feed Recovered
#1	2 vol.%	2034	256	87	92%
	4 vol.%	2034	190	91	91%
	10 vol.%	2034	37	98	69%

EXAMPLE 2

[0026] The same virgin gas oil feedstream of Example 1 was treated according to the method outlined in Example 1 above. In this experiment, however, the sulfuric acid solution mixed with the virgin gas oil was a spent sulfuric acid recovered from an alkylation process unit, referred to herein as acid solution #2. The spent sulfuric acid had a composition of 90 wt.% sulfuric acid, 4 wt.% water and 6 wt.% acid soluble hydrocarbon. This converts to an equivalent sulfuric acid strength as defined above of 96 wt.%. The virgin gas oil feedstream was separately mixed with 1 ml (5 vol.% treat rate) and 20 ml (10 vol.% treat rate) of sulfuric acid solution #1 and sulfuric acid solution #2, respectively. The results of this experiment are contained in Table 2 below, which compares the results of treatment with sulfuric acid solution #1 and #2.

TABLE 2					
Acid Solution	Volumetric Treat Rate	wppm Nitrogen in Feed	wppm Nitrogen in Product	% Nitrogen Removal	Feed Recovered
#1	5 vol.%	2034	144	93	79%
	10 vol.%	2034	190	91	91%
#2	5 vol.%	2034	212	90	90%
	10 vol.%	2034	112	95	87%

[0027] As can be seen in Table 1, the feed responded well to treatment with both acid solutions. It is also noted that some advantage in feed recovery is achieved at the 5 vol.% treat rate with the spent sulfuric acid solution.

CLAIMS:

1. An improved catalytic cracking method comprising:
 - a) providing a sulfuric acid solution containing greater than about 75 wt.% sulfuric acid;
 - b) contacting a nitrogen-containing catalytic cracking boiling range feedstream with the sulfuric acid solution in a first reaction stage under effective conditions and at an acid solution volumetric treat rate greater than about 0.5 vol.%, based on the catalytic cracking boiling range feedstream, wherein greater than about 60 wt.% of the nitrogen compounds contained in said catalytic cracking boiling range feedstream is removed thereby producing a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution; and
 - c) conducting at least a portion of said first reaction stage effluent to a second reaction stage wherein said first reaction stage effluent is contacted under effective cracking conditions with a cracking catalyst
2. The method according to claim 1 wherein the nitrogen-containing catalytic cracking boiling range feedstream boils in the range of about 430°F to about 1050°F (220-565°C).
3. The method according to any preceding claim wherein nitrogen-containing catalytic cracking boiling range feedstream comprises heavy hydrocarbon oils comprising materials boiling above 1050°F (565°C); heavy and reduced petroleum crude oil; petroleum atmospheric distillation bottoms;

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petroleum vacuum distillation bottoms; pitch, asphalt, bitumen, other heavy hydrocarbon residues; tar sand oils; shale oil; liquid products derived from coal liquefaction processes; light or heavy cycle oils; and mixtures thereof.

4. The method according to any preceding claim wherein the nitrogen-containing catalytic cracking boiling range feedstream comprises vacuum gas oils boiling in the range above about 650°F (343°C).
5. The method according to any preceding claim wherein the nitrogen-containing catalytic cracking boiling range feedstream contains about 100 to about 10,000 wppm nitrogen.
6. The method according to any preceding claim wherein the nitrogen-containing catalytic cracking boiling range feedstreams has a total metals concentration ranging from about 10 wppm to about 1,000 wppm.
7. The method according to any preceding claim wherein the nitrogen present in said nitrogen-containing catalytic cracking boiling range feedstream are selected from quinolines, substituted quinolines, benzo quinolines, anilines, N-alkyl indoles, alkylaryl amines and substituted derivatives thereof, indoles, and carbazoles.
8. The method according to any preceding claim wherein said sulfuric acid solution contains greater than about 80 wt.% sulfuric acid.

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9. The method according to any preceding claim wherein said sulfuric acid solution is a sulfuric acid solution obtained by:

- a) combining an olefinic hydrocarbon feedstream containing C₃ to C₅ 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.%.

10. The method according to any preceding claim wherein greater than about 75 wt.% of the nitrogen compounds contained in said catalytic cracking boiling range feedstream is removed.

11. The method according to any preceding claim wherein the treat rate of the sulfuric acid solution is about 0.5 to about 20 vol.%.

12. The method according to any preceding claim wherein the nitrogen-containing catalytic cracking boiling range feedstream and the sulfuric acid solution are intimately contacted by a non-dispersive contacting method selected from packed beds of inert particles and fiber film contactors.

13. The method according to any preceding claim wherein the nitrogen-containing catalytic cracking boiling range feedstream and the sulfuric acid solution are intimately contacted by a method selected from mixing valves,

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mixing tanks or vessels, propeller mixers, in-line static mixers, and orifice plates.

14. The method according to any preceding claim wherein the first reaction stage effluent is separated into at least a catalytic cracking boiling range effluent and a used sulfuric acid solution by any means known to be effective at separating an acid from a hydrocarbon stream.

15. The method according to any preceding claim wherein the catalytic cracking boiling range effluent and the used sulfuric acid solution are separated by a separation device selected from settling tanks or drums, coalescers, electrostatic precipitators, or other similar device.

16. The method according to any preceding claim wherein the catalytic cracking boiling range effluent and the used sulfuric acid solution are separated by fiber film contactors.

17. The method according to any preceding claim wherein the catalytic cracking boiling range effluent has a lower total metals concentration than the cat cracker boiling range feedstream.

18. The method according to any preceding claim wherein the catalytic cracking boiling range effluent has a total metals concentration ranging from about 20 wppm to about 1000 wppm.

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19. The method 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.

20. The method according to any preceding claim wherein the sulfur content of said catalytic cracking boiling range effluent is about 0.1 to about 25 % lower than the cat cracker boiling range feedstream.

21. The method according to any preceding claim wherein the yield loss resulting from the sulfuric acid solution treatment is about 0.5 to about 30 wt.%.

22. An improved catalytic cracking method involving removing nitrogen from a nitrogen-containing catalytic cracking boiling range feedstream comprising:

- a) providing a sulfuric acid solution containing greater than about 80 wt.% sulfuric acid;
- b) contacting a nitrogen-containing catalytic cracking boiling range feedstream boiling in the range of about 430°F to about 1050°F (220-565°C) in a first reaction stage with a sulfuric acid solution under effective conditions and at an acid volumetric treat rate of about 0.5 to about 20 vol.%, based on the catalytic cracking boiling range feedstream, thereby producing a first reaction stage effluent comprising at least a catalytic cracking boiling range effluent and a used sulfuric acid solution, whereby greater than about 75 wt.% of the nitrogen compounds contained in said

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catalytic cracking boiling range feedstream is removed and said contacting is achieved through the use of a contacting method selected from non-dispersive and dispersive contacting methods; and

- c) conducting at least a portion of said first reaction stage effluent to a reaction stage wherein said first reaction stage effluent is contacted under effective cracking conditions with a cracking catalyst.