IMPROVED SELECTIVE CRACKED NAPHTHA DESULFURIZATION USING ARSENIC TRAP CATALYSTS

FIELD OF THE INVENTION

[0001] This invention provides a process for the manufacture of a naphtha boiling range product with improved properties.

BACKGROUND OF THE INVENTION

[0002] One conventional technique for processing of cracked naphthas involves performing a selective hydrodesulfurization of the cracked naphtha. A selective hydrodesulfurization refers to a process where sulfur is removed from the naphtha while minimizing the amount of olefin saturation that occurs in the reaction. Avoiding olefin saturation can be valuable, as it leads to a higher octane naphtha product. Retaining a higher octane value allows a selectively hydrodesulfurized feed to be used as a naphtha fuel stock without having to use a reforming step.

[0003] One type of naphtha feed with a suitable octane rating for use without reforming is a naphtha feed produced by a fluid catalytic cracking (FCC) process. FCC naphtha feeds can contain a substantial amount of olefins, making a selective hydrodesulfurization process an attractive option. However, depending on the type of feed provided to the FCC process, the resulting FCC naphtha feed can also contain substantial amounts of arsenic. Arsenic is a known catalyst poison for many hydrodesulfurization catalysts.

[0004] Arsenic trap catalysts are commercially available for mitigating the effects of arsenic in a feed. In the present invention, such arsenic trap catalysts can be loaded at or near the top of the catalyst bed(s) for a hydrodesulfurization process. The arsenic trap catalyst can function to sequester arsenic from the feed, thereby reducing or even preventing the arsenic from reaching, and subsequently poisoning the hydrodesulfurization catalyst.

SUMMARY OF THE INVENTION

[0005] One aspect of the invention relates to a method for selectively hydrotreating a naphtha boiling range feed that includes providing a naphtha boiling range feed containing at least about 5 wt% olefins and at least about 1 ppb of arsenic. A run length and product sulfur content for the selective hydrodesulfurization process can then be identified. Additionally, first effective selective hydrodesulfurization conditions can be determined for selectively hydrodesulfurizing the naphtha boiling range feed in the presence of a first volume of hydrodesulfurization catalyst, with the first effective conditions including a first start of run catalyst bed temperature and a first space velocity. The naphtha boiling range feed can then be contacted with an arsenic trap catalyst. This can be followed by contacting the naphtha boiling range feed with a second volume of hydrodesulfurization catalyst that is about 95% or less of the first volume under the second effective selective hydrodesulfurization conditions, with the second effective selective hydrodesulfurization conditions including (i) a second start of run catalyst bed temperature that is at least about 1.5°C higher than the first start of run catalyst bed temperature and (ii) a second space velocity that is greater than the first space velocity. In this aspect of the invention, the naphtha boiling range feed can contact the arsenic trap catalyst prior to contacting the second volume of hydrodesulfurization catalyst. The contacting of the naphtha boiling range feed with the arsenic trap catalyst and the second volume of hydrodesulfurization catalyst can be continued for the identified run length while maintaining the identified product sulfur content in the hydrodesulfurized naphtha feed.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 schematically shows an example of a reactor suitable for performing an embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0007] In an embodiment, a low cost process is provided for producing naphtha boiling range products with at least comparable, and preferably improved, octane while achieving a desired process run length. The improved octane preservation can be achieved by using a combination of a reduced hydrodesulfurization catalyst load with a sufficient load of As trap catalyst to match a desired run length. This can allow the hydrodesulfurization reactor to be operated at a higher initial temperature, which can enhance octane preservation during the early portions of the run length for a hydrodesulfurization process.

[0008] In a selective hydrodesulfurization process, a variety of considerations can be balanced in order to choose the size of the catalyst load and the processing temperature. It can often be desirable to remove sulfur to a level that corresponds to the current requirements for low sulfur fuels. For example, production of a naphtha product with about 15 wppm or less, for example about 10 wppm or less, of sulfur is often desirable. Another consideration can include maintaining the activity of the catalyst. Typically, a catalyst should deactivate more quickly during higher temperature operation. Thus, lower operating temperatures can be preferred, particularly during the initial processing period after new catalyst has been added to a hydroprocessing reactor. Still another consideration can include preservation of olefins in the resulting naphtha product. Often, processing a feed at a temperature that is higher than necessary to meet a desired sulfur specification can result in additional saturation of olefins. This consideration would tend to suggest that lower reaction temperatures are preferable, to avoid overprocessing of a feed. However, the selectivity of a catalyst can increase with increasing temperature. Here, selectivity refers to the relative activity for hydrodesulfurization versus activity for olefin saturation. Thus, there are factors that can favor both lower and higher temperature processing.

[0009] Contaminants in a feed can provide another set of challenges for consideration. A catalyst poison such as arsenic can reduce the activity of a hydrodesulfurization catalyst during the course of a hydrodesulfurization process. The arsenic can often cause the catalyst to deactivate at a much faster rate than would typically be expected. One method to combat this deactivation includes increasing the overall catalyst load. Due to practical considerations, end of run temperatures above about 800°F (about 427°C) are typically not preferred, and preferably the end of run temperature can be less than about 675°F (about 357°C). Increasing the amount of hydrodesulfurization catalyst can reduce the temperature required to effectively hydrodesulfurize a given flow rate of a naphtha feed. By increasing the amount of hydrodesulfurization catalyst, a portion of the catalyst can be deactivated while still leaving sufficient higher activity catalyst to stay below a desired temperature for a desired run length.

[0010] Conventionally, increased catalyst loads have been used in conjunction with arsenic trap catalysts. An arsenic trap catalyst can be loaded into a catalyst bed so that the feed contacts the arsenic trap catalyst prior to contacting the hydrodesulfurization catalyst(s) in the reactor. Without wishing to be bound by theory, it is believed that the hydrodesulfurization catalyst binds with the arsenic, thus reducing the amount of arsenic from reaching the hydrodesulfurization catalyst and extending the run length for a reactor, as the hydrodesulfurization catalyst would undergo only typical deactivation from processing, and not more rapid deactivation due to the presence of arsenic.

[0011] In contrast to a conventional use of an arsenic trap catalyst, various embodiments of the invention make use of an arsenic trap catalyst to maintain, and preferably enhance, the octane value of the desulfurized naphtha product. This can be achieved by reducing the amount of hydrodesulfurization catalyst used. By using less catalyst, the start of run temperature for the reaction can be increased, which can allow for greater octane retention. In an embodiment, use

of an arsenic trap catalyst can allow the volume of hydrodesulfurization catalyst to be reduced to about 95% or less of the volume required without the arsenic trap catalyst, for example to about 90% or less or to about 85% or less. By reducing the volume of hydrodesulfurization catalyst, the corresponding space velocity for feed contacting the hydrodesulfurization catalyst can be increased while still processing a similar flow rate of feed. In an embodiment, use of an arsenic trap catalyst can allow a space velocity that is greater than the space velocity without the use of an arsenic trap catalyst. Preferably, the space velocity with the arsenic trap catalyst can be at least about 105% of the space velocity without the arsenic trap catalyst, for example at least about 110% of the space velocity without the arsenic trap catalyst.

Feedstocks

[0012] In various embodiments, the feedstock for a selective hydrodesulfurization process can be a naphtha boiling range feed, particularly an olefinic naphtha boiling range feed. Suitable feedstocks can typically boil in the range from about 50°F (about 10°C) to about 450°F (about 232°C). With regard to olefin content, suitable feedstocks can advantageously include feedstocks having an olefin content of at least about 5 wt%. Non-limiting examples of such suitable feedstocks can include, but are by no means limited to, fluid catalytic cracking unit naphtha (FCC catalytic naphtha or cat naphtha), steam cracked naphtha, coker naphtha, or a combination thereof. Also included are blends of olefinic naphthas with non-olefinic naphthas, so long as the blend has an olefin content of at least about 5 wt%.

[0013] Olefinic naphtha refinery streams generally contain not only paraffins, naphthenes, and aromatics, but also unsaturates, such as open-chain and cyclic olefins, dienes, and cyclic hydrocarbons with olefinic side chains. The olefinic naphtha feedstock can contain an overall olefins concentration of about 60 wt% or less, for example about 50 wt% or less or about 40 wt% or less. Additionally or alternately, the olefin concentration can be at least about 5 wt%,

for example at least about 10 wt% or at least about 20 wt%. The olefinic naphtha feedstock can also have a diene concentration up to about 15 wt%, but more typically less than about 5 wt%, based on the total weight of the feedstock. High diene concentrations are typically undesirable, since they can result in a gasoline product having poor stability and color.

[0014] The sulfur content of the olefinic naphtha can be at least about 100 wppm, for example at least about 500 wppm, at least about 1000 wppm, or at least about 1500 wppm. Additionally or alternately, the sulfur content can be about 7000 wppm or less, for example about 6000 wppm or less, about 5000 wppm or less, or about 3000 wppm or less. The sulfur can typically be present as organically bound sulfur, *i.e.*, as sulfur compounds such as simple aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and poly- sulfides, and the like. Other organically bound sulfur compounds can include the class of heterocyclic sulfur compounds such as thiophene and its higher homologs/analogs (including dibenzodithiophene *et al.*).

[0015] Nitrogen can also be present in the feed. In an embodiment, the amount of nitrogen can be at least about 5 wppm, for example at least about 10 wppm, at least about 20 wppm, or at least about 40 wppm. Additionally or alternately, the nitrogen content can be about 250 wppm or less, for example about 150 wppm or less, about 100 wppm or less, or about 50 wppm or less.

[0016] Arsenic can also be present in the feed. In an embodiment, the amount of arsenic can be at least about 1 wppb, for example at least about 5 wppb, at least about 10 wppb, at least about 20 wppb, or at least about 40 wppb. Additionally or alternately, the arsenic content can be about 100 wppb or less, for example about 75 wppb or less or about 50 wppb or less.

Catalysts

[0017] A selective hydrodesulfurization can be performed by exposing an olefinic naphtha feed to one or more beds of hydrodesulfurization catalyst under effective selective hydrodesulfurization conditions. In an embodiment, an arsenic trap catalyst can be used in a separate bed, such as a bed that is upstream of the hydrodesulfurization catalyst bed(s), or the arsenic trap catalyst can be loaded into the top of a bed that also includes a hydrodesulfurization catalyst.

[0018] Typically, arsenic trap catalysts are catalysts with sufficient activity to sequester (adsorb) arsenic, but with otherwise a relatively low catalytic activity that has a reduced or minimal impact on the desired reaction, such as hydrodesulfurization. Typical arsenic trap catalysts can be relatively low activity supported nickel-based catalysts. For example, a catalyst could include from about 5 wt% to about 20 wt% of Ni on an alumina support. A commercially available example of such an arsenic trap catalyst includes TK-47, which is commercially available from Haldor Topsoe.

[0019] In an embodiment, the amount of arsenic trap catalyst to include in the catalyst beds can be dependent on the amount of arsenic present in the feed, as well as on the desired run length. Preferably, the amount of arsenic trap catalyst can be sufficient to prevent substantial arsenic contact with the hydrodesulfurization catalyst. It is noted that having an excess of arsenic trap catalyst can have little or no effect (other than increased catalyst cost) on hydrodesulfurization activity and/or selectivity, as the arsenic trap catalyst can typically have a relatively low activity for hydrodesulfurization and/or olefin saturation.

[0020] In various embodiments, suitable selective hydrodesulfurization catalysts can include catalysts that are comprised of: at least one Group VIII metal oxide, for example an oxide Co and/or Ni, preferably at least containing Co; and at least one Group VIB metal oxide, for example an oxide of Mo and/or

W, preferably at least containing Mo; on a support material, such as silica, alumina, or a combination thereof. Other suitable hydrotreating catalysts can include zeolitic catalysts, as well as noble metal catalysts (*e.g.*, where the noble metal comprises Pd and/or Pt). It is within the scope of the present invention that more than one type of hydrotreating catalyst be used in the same reaction vessel. The Group VIII metal oxide of a selective hydrodesulfurization catalyst can be present in an amount ranging from about 0.1 wt% to about 20 wt%, preferably from about 1 wt% to about 12%. Additionally or alternately, the Group VIB metal oxide can be present in an amount ranging from about 1 wt% to about 50 wt%, preferably from about 2 wt% to about 20 wt%. All metal oxide weight percents are on support. By "on support," it is meant that the percents are based on the weight of the support. For example, if the support were to weigh 100 grams, then 20 wt% Group VIII metal oxide would mean that 20 grams of Group VIII metal oxide is on the support.

[0021] The hydrodesulfurization catalysts used in the practice of the present invention can preferably be supported catalysts. Any suitable refractory catalyst support material, preferably inorganic oxide support materials, can be used as supports for the catalyst of the present invention. Non-limiting examples of suitable support materials can include zeolites, alumina, silica, titania, calcium oxide, strontium oxide, barium oxide, carbon, zirconia, magnesia, diatomaceous earth, lanthanide oxides (including cerium oxide, lanthanum oxide, neodymium oxide, yttrium oxide, and praesodymium oxide), chromia, thorium oxide, urania, niobia, tantala, tin oxide, zinc oxide, aluminum phosphates, and the like, and combinations thereof. Preferred supports include alumina, silica, and silica-alumina. It is to be understood that the support material can also contain small amounts of contaminants, such as Fe, sulfates, silica, and/or various metal oxides that can be introduced during the preparation of the support material. These contaminants can often be present in the raw materials used to prepare the support and can preferably be present in amounts less than about 1 wt%, based

on the total weight of the support. It is more preferred that the support material be substantially free (*e.g.*, containing not more than about 0.1 wt%, preferably not more than about 0.05 wt%, not more than about 0.01 wt%, or no detectable amount) of such contaminants. Additionally or alternately, about 0 wt% to about 5 wt%, for example from about 0.5 wt% to about 4 wt% or from about 1 wt% to about 3 wt%, of an additive can be present in/on the support, which additive can be selected from the group consisting of phosphorus and metals or metal oxides from Group IA (alkali metals) of the (CAS version of the) Periodic Table of the Elements.

Reaction conditions and environment

[0022] The selective hydrodesulfurization can be performed in any suitable reaction system, for instance in one or more fixed bed reactors, each of which can comprise one or more catalyst beds of the same, or different, hydrodesulfurization catalyst. Optionally, more than one type of catalyst can be used in a single bed. Although other types of catalyst beds can be used, fixed beds are preferred. Non-limiting examples of such other types of catalyst beds that may be used in the practice of the present invention can include, but are not limited to, fluidized beds, ebullating beds, slurry beds, moving beds, and the like, and combinations thereof. Interstage cooling between reactors, or between catalyst beds in the same reactor, can be employed in some embodiments, since some olefin saturation can take place, and since olefin saturation, as well as desulfurization, are generally exothermic. A portion of the heat generated during hydrodesulfurization can be recovered, *e.g.*, by conventional techniques. Where this heat recovery option is not available, conventional cooling may be performed through cooling utilities such as cooling water or air, and/or by use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained.

[0023] Generally, selective hydrodesulfurization conditions can include a temperature from about 425°F (about 218°C) to about 800°F (about 427°C),

preferably from about 500°F (about 260°C) to about 675°F (about 357°C). In an embodiment, the temperature at the start of a reaction run can be at least about 450°F (about 232°C), for example at least about 475°F (about 246°C), at least about 500°F (about 260°C), or at least about 510°F (about 266°C). Additionally or alternately, the temperature at the start of a run can be about 575°F (about 302°C) or less, for example about 540°F (about 282°C) or less or about 525°F (about 274°C) or less.

[0024] Independently, or in combination with the embodiments describing the start of run temperature, the temperature at the end of a processing run can be about 800°F (about 427°C) or less, for example about 750°F (about 399°C) or less, about 700°F (about 371°C) or less, about 675°F (about 357°C) or less, or about 650°F (about 343°C) or less. Additionally or alternately, the temperature at the end of a processing run can be at least about 550°F (about 288°C), for example at least about 575°F (about 302°C), at least about 600°F (about 316°C), or at least about 625°F (about 329°C).

[0025] In various embodiments, the temperature selected as the end of a processing run can be dependent on a variety of factors. For example, it could be desirable to operate the reactor and other equipment in a reaction system at temperatures below a certain value. This could be due to equipment limitations, a desired temperature in another upstream or downstream process, or for other reasons. Another consideration can be the rate of catalyst deactivation. As a catalyst deactivates, the number of remaining active sites on catalyst can be reduced. When many of the active sites on a catalyst are deactivated, the process stability for using the catalyst can be reduced. This could be reflected, for example, in a need to increase temperature at a faster rate in order to maintain a substantially constant sulfur level. Additionally, as noted above, some types of catalysts generally deactivate more quickly at higher temperatures.

[0026] In an embodiment, the temperature differential between the beginning of a hydrodesulfurization process and the end of the process can be at

least about 25°F (about 14°C), for example at least about 50°F (about 28°C), at least about 75°F (about 42°C), or at least about 100°F (about 56°C). Additionally or alternately, the temperature differential between the start of a run and the end of a run can be about 300°F (about 167°C) or less, for example about 200°F (about 111°C) or less, about 150°F (about 83°C) or less, about 100°F (about 56°C) or less, or about 75°F (about 42°C) or less.

[0027] Other selective hydrodesulfurization conditions can include a pressure from about 60 psig (about 400 kPag) to about 800 psig (about 5.5 MPag), for example from about 200 psig (about 1.4 MPag) to about 500 psig (about 3.4 MPag) or from about 250 psig (about 1.7 MPag) to about 400 psig (about 2.8 MPag). The hydrogen feed rate can be from about 500 scf/b (about 84 Nm^3/m^3) to about 6000 scf/b (about 1000 Nm^3/m^3), for example from about 1000 scf/b (about 170 Nm^3/m^3) to about 3000 scf/b (about 510 Nm^3/m^3). The liquid hourly space velocity can be from about 0.5 hr^{-1} to about 15 hr^{-1}, for example from about 0.5 hr^{-1} to about 10 hr^{-1} or from about 1 hr^{-1} to about 5 hr^{-1}.

[0028] FIG. 1 schematically shows an example of a reactor suitable for performing an embodiment of the invention. In FIG. 1, an arsenic-containing naphtha feed 105 and a hydrogen feed 107 are introduced into a reactor 110. Reactor 110 is shown as including a separate arsenic trap catalyst bed 112 and a separate hydrodesulfurization catalyst bed 114. Alternately, the arsenic trap catalyst and hydrodesulfurization catalyst can be in a single bed, with the arsenic trap catalyst loaded at the top of the bed. Optionally, additional hydrodesulfurization catalyst beds 114 could also be included. After treatment in reactor 110, the hydrodesulfurized feed 115 can be passed to a separator 120. In the embodiment shown in FIG. 1, separator 120 can advantageously remove a stream 127 comprising H_2, H_2S, and other gas phase products from the rest of the separated, desulfurized naphtha feed 125.

Product Characterization and Control of Reaction Conditions

[0029] In various embodiments, a hydrotreated naphtha can be produced with reduced or preferably no loss of octane, as compared to a hydrotreated naphtha formed from a similar process that does not employ an arsenic trap catalyst. By allowing use of reduced amount of catalyst, and therefore an increased start of run temperature, olefin saturation can be reduced. This can lead to higher values for the road octane number (RON) and/or the motor octane number (MON) for the resulting hydrotreated naphtha.

[0030] In various embodiments, a goal of a selective hydrodesulfurization process can be to produce a naphtha product having a substantially constant level of sulfur. In an embodiment, the substantially constant level of sulfur can be at least about 5 wppm, for example at least about 10 wppm, at least about 15 wppm, at least about 20 wppm, or at least about 30 wppm. Additionally or alternately, the substantially constant level of sulfur can be about 150 wppm or less, for example about 100 wppm or less, about 75 wppm or less, about 50 wppm or less, or about 30 wppm or less. As used herein, maintaining a substantially constant level of sulfur in a hydrodesulfurized product can be defined as maintaining the sulfur content to within about 5 wppm (*e.g.*, to within about 3 wppm) of the target level.

[0031] It can be desirable to maintain a substantially constant level of sulfur in the naphtha product for a variety of reasons. Maintaining a constant level of sulfur can allow for process control, as a gasoline formulator will be able to rely on the specifications for the naphtha product. For this purpose, maintaining a substantially constant sulfur level can be beneficial, because the sulfur content does not increase. It can also be desirable to provide a constant sulfur level to prevent the sulfur level from being too low. At the product sulfur levels described for embodiments of this invention, removing additional sulfur can indicate that the reaction conditions may be too severe. Using more severe hydrodesulfurization conditions can sometimes result in increased saturation of

olefin bonds, which may be undesirable. Thus, achieving a sulfur level that is lower than the target level can actually be detrimental in some instances, as the processing used to achieve the lower sulfur level may also further reduce the RON and or MON of the naphtha product.

[0032] In various embodiments, another goal can be to provide a naphtha product with an improved octane number. By operating at a higher start of run temperature but with a reduced catalyst amount (*e.g.*, so that the feed is not over-processed), fewer olefin bonds can be saturated in the feed and/or converted into mercaptans. Such preservation of olefins can lead to reduced octane loss during hydrodesulfurization. In an embodiment, the octane loss due to hydrodesulfurization can be reduced by about 0.05 RON or more, for example by about 0.1 RON or more, relative to the octane loss due to hydrodesulfurization under similar conditions without an arsenic trap catalyst.

[0033] One or both of the aforementioned goals may be attained according to the invention, or neither of the goals may be attained.

[0034] One way to maintain a desired sulfur level can be to use the product sulfur level to provide feedback for the process conditions. Various methods are available for detecting product sulfur levels. One option for monitoring sulfur levels can be to withdraw samples of the hydrodesulfurized naphtha and analyze the sample for sulfur. Due to the time scales involved in catalyst deactivation during processing, off-line analysis of a naphtha sample can be sufficient to allow for maintaining a substantially constant level. Alternately, techniques for in-line monitoring of sulfur content levels in a hydrodesulfurized naphtha product may also be available. While in certain circumstances it may be desirable to use a system containing an arsenic trap catalyst in order to reduce the product sulfur content, in other circumstances feedback based on the sulfur level in the naphtha product can be used to adjust reaction conditions so that a substantially constant level of product sulfur can be maintained. In various embodiments, adjusting the reaction conditions can include adjusting the

temperature of the catalyst bed (the Weighted Average Bed Temperature), *inter alia*.

Example – Simulation of Selective Hydrotreating with and without Arsenic Trap

[0035] Process simulations for a selective hydrodesulfurization process were developed to illustrate an advantage of using arsenic trap catalyst. The simulation results are shown in Table 1. The conditions for these simulations included: about 5500 barrels/day (about 870 m^3/day) of FCC naphtha feed; about 4200 wppm feed sulfur content; about 45 centigrams/gram feed bromine number; and about 40 ppb feed arsenic content. One process objective was to lower the sulfur content to at least about 120 wppm, while meeting an approximate six year run length. The treat gas rate was about 620000 scf/hr (about 18000 Nm^3/hr), with about 72% hydrogen and about 10 wppm CO (remainder inert gas). The catalyst being simulated represented commercially available CoMo catalyst on a refractory support.

Table 1

	Units	Zero As Trap	Full Run Length As Trap
As Trap Volume	m^3	N/A	2.0
As Trap LHSV	hr^{-1}	N/A	18
As Trap run length (based on 40 ppb feed)	years	N/A	6.1
Catalyst Volume	m^3	57.9	48.6
Catalyst LHSV	hr^{-1}	0.63	0.75
End of Run Catalyst As (based on 40 ppb feed)	wt%	0.2	0.0
Catalyst Bed WABT (SOR)	°C	261	264
RON loss		8.52	8.40
Product sulfur	ppm	120	120

[0036] The first data column in Table 1 (Zero As Trap) shows that a catalyst volume of about 2043 ft^3 (about 57.9 m^3) was required to meet the run length objective of approximately six years. The expected start of run (SOR) temperature was about 502°F (about 261°C). The second data column shows that, by adding about 71.5 ft^3 (about 2.0 m^3) of arsenic trap catalyst, the same run length could be achieved with a lower catalyst volume of about 1716 ft^3 (about

48.6 m^3) while reducing octane loss by about 0.12 RON (road octane number). The higher SOR temperature for the second case of 508°F (about 264°C) appeared to reduce mercaptan formation and to improve octane loss. The higher SOR temperature would ordinarily result in faster deactivation, but this is balanced out by the presence of arsenic trap catalyst, which mitigates arsenic-based deactivation. It is noted that the amount of arsenic trap catalyst in the second data column was roughly equivalent to that needed to minimize the arsenic from reaching the main catalyst bed. This was indicated by the expected arsenic trap run length of about 6.1 years.

CLAIMS:

1. A method for selectively hydrotreating a naphtha boiling range feed, comprising:

providing a naphtha boiling range feed containing at least about 5 wt% olefins and at least about 1 ppb arsenic;

identifying a run length and product sulfur content for a selective hydrodesulfurization process;

determining first effective selective hydrodesulfurization conditions for selectively hydrodesulfurizing the naphtha boiling range feed in the presence of a first volume of hydrodesulfurization catalyst, the first effective conditions including a first start of run catalyst bed temperature and a first space velocity;

contacting the naphtha boiling range feed with an arsenic trap catalyst; and

contacting the naphtha boiling range feed with a second volume of hydrodesulfurization catalyst that is about 95% or less of the first volume under the second effective selective hydrodesulfurization conditions, the second effective selective hydrodesulfurization conditions including a second start of run catalyst bed temperature that is at least about 1.5°C higher than the first start of run catalyst bed temperature, and a second space velocity that is greater than the first space velocity;

wherein the naphtha boiling range feed contacts the arsenic trap catalyst prior to contacting the second volume of hydrodesulfurization catalyst, and further wherein the contacting of the naphtha boiling range feed with the arsenic trap catalyst and the second volume of hydrodesulfurization catalyst is continued for the identified run length while maintaining the identified product sulfur content in the hydrodesulfurized naphtha feed.

2. The method of claim 1, wherein the second volume of catalyst is about 90% or less of the first volume.

3. The method of claim 1 or claim 2, wherein the second space velocity is about 105% of the first space velocity.

4. The method of any of the above claims, wherein the second start of run catalyst bed temperature is at least about 2.5°C higher than the first start of run catalyst bed temperature.

5. The method of any of the above claims, wherein the identified product sulfur content is less than about 150 wppm.

6. The method of any of the above claims, wherein the identified product sulfur content is from about 10 wppm to about 30 wppm.

7. The method of any of the above claims, wherein the start of run catalyst bed temperature is from about 450°F (about 232°C) to about 575°F (about 302°C).

8. The method of any of the above claims, wherein the weighted average bed temperature at an end of the contacting of the hydrodesulfurization catalyst is from about 550°F (about 288°C) to 750°F (about 399°C).

9. The method of any of the above claims, wherein the second effective selective hydrodesulfurization conditions include a pressure from about 60 psig (about 400 kPag) to about 800 psig (about 5.5 MPag), a hydrogen feed rate from about 500 standard cubic feet per barrel (scf/b) (about 84 Nm^3/m^3) to about 6000 scf/b (about 1000 Nm^3/m^3), and a liquid hourly space velocity from about 0.5 hr^{-1} to about 15 hr^{-1}.

10. The method of any of the above claims, wherein the second effective selective hydrodesulfurization conditions include a pressure from about 200 psig (about 1.4 MPag) to about 500 psig (about 3.4 MPag), a hydrogen feed

rate from about 1000 scf/b (about 170 Nm^3/m^3) to about 3000 scf/b (about 510 Nm^3/m^3), and a liquid hourly space velocity from about 0.5 hr^{-1} to about 10 hr^{-1}.

11. The method of any of the above claims, wherein contacting the naphtha feed with the second volume of hydrodesulfurization catalyst under the second effective hydrodesulfurization conditions results in a loss of octane number that is at least 0.05 RON less than a corresponding loss of octane number due to contacting the naphtha feed with the first volume of hydrodesulfurization catalyst under the first effective hydrodesulfurization conditions.

12. The method of any of the above claims, wherein the naphtha boiling range feed includes at least about 10 ppb arsenic, preferably at least about 20 ppb arsenic.