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(54) Title: DESULFURIZATION OF A NAPHTHA BOILING RANGE FEED

(57) Abstract: Processes for desulfurizing a fluid catalytic cracker (FCC) naphtha feedstock, straight run naphtha feedstocks and combinations thereof are provided herein. Naphtha boiling range feed is passed over a silicon trap prior to being hydrodesulfurized in an olefin-retentive, catalytic naphtha hydrodesulfunzation process. Processes for removing silicon from FCC naphtha feedstock, straight run naphtha feedstock and combinations thereof are also provided herein.

DESULFURIZATION OF A NAPHTHA BOILING RANGE FEED

FIELD

[0001] This invention relates to methods of desulfurizing fluid catalytic cracker (FCC) naphtha feedstocks, straight run naphtha feedstocks and combinations thereof for effective use in the refinery gasoline pool.

BACKGROUND

[0002] A large proportion of the gasoline pool in the United States, Europe and elsewhere is filled by naphtha from fluid catalytic cracking units. While this naphtha has good octane as a result of a relatively high olefin content resulting from the catalytic cracking process, it also tends to have an unacceptably high sulfur content under the regulatory standards for motor gasoline (mogas). Sulfur specifications on the order of less than 150 wppm of total sulfur are likely near term, with values of no greater than 10 wppm of total sulfur possible in the not too distant future. Over the same time period, the progressive decreases in permitted sulfur content have been accompanied by a requirement to reduce mobile source emissions, especially carbon monoxide, by the addition of oxygenates, usually provided in the form of bioethanol, since the use of ether-type oxygenates, such as methyl tertiary butyl ether (MTBE), became controversial in the United States and legislation favoring ethanol became effective.

[0003] Ethanol has a high octane number, commonly reported as about 108 RON (Research Octane Number) but some reports from ethanol manufacturers place it as high as 113 RON although not specifying the MON (Motor Octane Number). However, it is accepted that blending ethanol with gasoline will have a favorable effect on the RON so that there may be little difficulty for the refiner to meet the PON (Pump Octane Number) requirements of most vehicles with ethanol blends. The octane boost provided by the use of ethanol in gasoline blends, typically an E10 blend with 10 percent ethanol has provided an opportunity to bring feedstocks previously considered of marginal acceptability into the refinery pool for processing into motor gasoline.

[0004] FCC naphtha, being derived by the catalytic cracking of high boiling, high-molecular weight hydrocarbons may generally have a higher sulfur content as well as olefin content, although its octane may be lower. Retention of olefins is therefore necessary if octane targets in the gasoline pool are to be met; in addition, sulfur must be significantly reduced to meet current and future sulfur limits in the gasoline pool.

[0005] A number of sulfur reduction techniques for gasoline blend components have been developed, summarized briefly in US Patent No. 7,837,861. The ExxonMobil selective naphtha hydrofining process, SCANfining™, developed for deep hydrodesulfurization (HDS) with maximum preservation of the olefins (octane), which is commercially available under license from

ExxonMobil Research and Engineering Company, is a very effective naphtha desulfurization process which incorporates aspects of the processes described in the following U.S. patents: US 5,985,136; US 6,231,753; 6,409,913; US 6,231,754; US 6,013,598; US. 6,387,249 and US 6,596,157. The single stage version of the process can be used with a full range catalytic naphtha or with an intermediate catalytic naphtha (ICN), for example a nominal 65–175°C (150–350°F) naphtha or a heavy catalytic naphtha (HCN), for example, a nominal 175°C+ (350°F+) naphtha, or both. The two-stage version of the process, as described in US Patent No. 6,231,753, and International Patent Publication Nos. WO 03/048273 and WO 03/099963, adds a second reactor and inter-stage removal of H_2S allowing very deep HDS with very good olefin retention. The operation of this process relies on a combination of a highly selective catalyst with process conditions designed to achieve hydrodesulfurization with minimum olefin saturation.

[0006] While the octane retention afforded by the HDS processes, such as the SCANfining process, is useful, difficulties may be encountered when the process stream intended for desulfurization contains silicon because silicon has been found to have a deleterious effect on HDS catalysts. As described in U.S. Patent Publication No. 2016/0046881, coker naphthas are expected to contain silicon. This silicon, in various combined forms, is generated from the silicone oil anti-foaming additives typically based on polydimethylsiloxane, used in the delayed coking process to suppress foaming caused by gas formation. The silicone oils may decompose in the coker naphtha to form modified silica gels and silicone fragments. The fragments are typically in the naphtha boiling range though some can boil at higher temperatures. The deactivating silica gels which have been found on catalyst surfaces have been primarily SiO_2, $Si(OSi)_4$, $Si(OSi)_3OH$ and methylated forms such as $=Si(CH_3)_2$. In downstream hydroprocessing units (*e.g.*, HDS units), the silicon-containing fragments from the anti-foam agent and/or the crude oil may undergo a condensation reaction with alumina surfaces of catalysts, forming a strong chemical bond. Once the silicon is bound to the alumina surface, it cannot usually be removed by regeneration or other means. The silicon may block the pore system of the catalyst and thus, access to the active sites thereby reducing activity of the catalyst as well as its ability to absorb other poisons, such as arsenic. For example, the presence of silicon on the catalysts may result in activity loss of the order of 5–10°F (3–6°C) for each 1.0 wt% Si deposited on the catalyst.

[0007] While it was known that coker naphthas contain silicon, it was unexpected that FCC naphthas and/or straight run naphthas can contain silicon as well. As described above, this unexpected presence of silicon in FCC naphthas and/or straight run naphthas can lead to undesirable loss of HDS catalyst activity when desulfurizing FCC naphthas and/or straight run naphthas. Thus, there is a need for desulfurization processes which can also remove silicon contaminants from FCC naphtha, straight run naphtha or blends thereof to avoid silicon poisoning of catalysts during hydroprocessing, such as the olefin retentive process as SCANfining.

SUMMARY

[0008] It has been found that FCC naphtha and/or straight run naphtha can be more effectively processed in the feedstocks for olefin retentive selective catalytic naphtha hydrodesulfurization processes if a suitably selected silicon trap is used. To minimize the octane loss which occurs in the process, a high surface area inert alumina with a controlled low metal content may be used.

[0009] Thus, according to the present invention, a process for desulfurizing a naphtha boiling range feed is provided. The process comprises contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha, or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent and hydrodesulfurizing at least a portion of the naphtha boiling range effluent, *e.g.*, in an olefin-retentive, catalytic naphtha hydrodesulfurization process. Unpromoted (no intentional metals content), inert alumina is preferred since it may not affect the olefin-retentive qualities of the hydrodesulfurization catalyst and for maximal silica capture, a high surface area alumina may be employed.

[0010] In another aspect, a process for removing silicon from a naphtha boiling range feed is provided comprising contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha, or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent and hydrodesulfurizing the naphtha boiling range effluent, *e.g.*, in an olefin-retentive, catalytic naphtha hydrodesulfurization process, wherein the inert alumina has: (i) a surface area of at least about 250 m^2/g; (ii) a particle size less than about 1.6 mm; and (iii) a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals and not more than about 5.0 wt% Group 6 metals.

DETAILED DESCRIPTION

I. Definitions

[0011] For purposes of this invention and the claims hereto, the numbering scheme for the Periodic Table Groups is according to the IUPAC Periodic Table of Elements.

[0012] The term “and/or” as used in a phrase such as “A and/or B” herein is intended to include “A and B”, “A or B”, “A”, and “B”.

[0013] As used herein, the phrase “at least a portion of” means > 0 to 100.0 wt% of the composition to which the phrase refers. The phrase “at least a portion of” refers to an amount ≤ about 1.0 wt%, ≤ about 2.0 wt%, ≤ about 5.0 wt%, ≤ about 10.0 wt%, ≤ about 20.0 wt%, ≤ about

25.0 wt%, ≤ about 30.0 wt%, ≤ about 40.0 wt%, ≤ about 50.0 wt%, ≤ about 60.0 wt%, ≤ about 70.0 wt%, ≤ about 75.0 wt%, ≤ about 80.0 wt%, ≤ about 90.0 wt%, ≤ about 95.0 wt%, ≤ about 98.0 wt%, ≤ about 99.0 wt%, or ≤ about 100.0 wt%. Additionally or alternatively, the phrase "at least a portion of" refers to an amount ≥ about 1.0 wt%, ≥ about 2.0 wt%, ≥ about 5.0 wt%, ≥ about 10.0 wt%, ≥ about 20.0 wt%, ≥ about 25.0 wt%, ≥ about 30.0 wt%, ≥ about 40.0 wt%, ≥ about 50.0 wt%, ≥ about 60.0 wt%, ≥ about 70.0 wt%, ≥ about 75.0 wt%, ≥ about 80.0 wt%, ≥ about 90.0 wt%, ≥ about 95.0 wt%, ≥ about 98.0 wt%, ≥ about 99.0 wt%, or about 100.0 wt%. Ranges expressly disclosed include combinations of any of the above-enumerated values; *e.g.*, about 10.0 to about 100.0 wt%, about 10.0 to about 98.0 wt%, about 2.0 to about 10.0 wt%, about 40.0 to 60.0 wt%, *etc*.

[0014] As used herein, and unless otherwise specified, the term "C_n" means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

[0015] As used herein, and unless otherwise specified, the term "hydrocarbon" means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n.

[0016] As used herein, the term "naphtha" or "naphtha boiling range" refers to a middle boiling range hydrocarbon fraction or fractions, typically including between about four and twelve carbon atoms, which are major components of gasoline. In one embodiment, naphtha or naphtha boiling range components is further defined to have a boiling range distribution between about 38°C and about 200°C at 0.101 MPa as measured according to ASTM D86, and further defined to meet ASTM standard D4814.

[0017] As used herein, the term "straight run naphtha" refers to petroleum naphtha obtained directly from fractional distillation.

[0018] As used herein, the term "fluid catalytic cracker (FCC) naphtha" refers to naphtha produced by the well-known process of fluid catalytic cracking.

II. Desulfurization Processes

[0019] As discussed herein, it was unexpectedly discovered that FCC naphtha and/or straight run naphtha streams can comprise silicon, which can poison downstream hydroprocessing catalysts. Thus processes are provided herein for desulfurizing a naphtha boiling range feed comprising contacting the naphtha boiling range with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent. The processes may further comprise hydrodesulfurizing the naphtha boiling range effluent.

II.A. Naphtha Boiling Range Feed

[0020] The naphtha boiling range feed in the desulfurization process may comprise, consist essentially of, or consist of FCC naphtha, straight run naphtha or a combination thereof. In some embodiments, the naphtha boiling range feed may comprise, consist essentially of, or consist of FCC naphtha or straight run naphtha in an amount (based on total weigh of the naphtha boiling range feed) of about 0.0 wt%, at least about 1.0 wt%, at least about 5.0 wt%, at least about 10 wt%, at least about 20 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, at least about 95 wt%, at least about 99 wt% or about 100 wt%. Additionally or alternatively, the naphtha boiling range feed may comprise, consist essentially of, or consist of FCC naphtha or straight run naphtha in an amount of about 0.0 wt% to about 100 wt%, about 1.0 wt% to about 100 wt%, about 20 wt% to about 100 wt%, about 50 wt% to about 100 wt%, about70 wt% to about 100 wt%, about 90 wt% to about 100 wt%, about 0.0 wt% to about 50 wt%, about 0.0 wt% to about 20 wt%, about 0.0 wt% to about 10 wt%, about 0.0 wt% to about 5.0 wt%, about 1.0 wt% to about 10 wt%, or about 1.0 wt% to about 5.0 wt%. In particular, where the naphtha boiling range feed includes less than about 100 wt% FCC naphtha, the balance of the naphtha boiling range feed may be straight run naphtha, and where the naphtha boiling range feed includes less than about 100 wt% straight run naphtha, the balance of the naphtha boiling range feed may be FCC naphtha. For example, the naphtha boiling range feed may comprise about 1.0 wt% to about 100 wt% FCC naphtha and about 0.0 wt% to about 99 wt% straight run naphtha or vice versa. Additionally or alternatively, the naphtha boiling range feed may comprise about 50 wt% to about 100 wt% FCC naphtha and about 0.0 wt% to about 50 wt% straight run naphtha or vice versa and so on.

[0021] In certain variations, the naphtha boiling range feed may comprise other components, such as a coker naphtha component from a delayed coker, or fluidized coker such as a Fluid Coker™, Flexicoker™, or others *e.g.*, in an amount of about 1.0 wt% to about 50 wt%, about 1.0 wt% to about 25 wt%, or about 1.0 wt% to about 10 wt%. In particular, the naptha boiling range feed may comprise FCC naphtha, straight run naphtha and coker naphtha.

[0022] In one embodiment, the naphtha boiling range feed may not include coker naphtha or delayed coker naphtha, which are derived from thermal cracking of residual feedstocks. Thus, in a particular embodiment, a process is provided for desulfurizing a naphtha boiling range feed comprising contacting the naphtha boiling range feed, which is not a coker naphtha or delayed coker naphtha, with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent and hydrodesulfurizing the naphtha boiling range effluent.

[0023] The naphtha boiling range feed may have various properties. For example, the naphtha boiling range feed may have an American Petroleum Institute (API) gravity, as measured according to ASTM D4052, of at least about 45, at least about 50, at least 55, at least about 60, at least about 65 or about 70, *e.g.*, about 58, about 60 or higher. Additionally or alternatively, the naphtha boiling range feed may have an API gravity, as measured according to ASTM D4052, of at least about 45 to about 70, about 50 to about 70 or about 55 to about 65.

[0024] Bromine number, representative of olefin content, of the naphtha boiling range feed may be typically from about 45 to about 80, about 50 to about 75, about 50 to about 70 or about 60, unless lowered by a significant amount of straight run naphtha. Bromine number may be measured according to ASTM D1159. Research Octane Number (RON), as measured according to ASTM D2699 and/or ASTM D2885, of the naphtha boiling range feed may be at least about 80, at least about 85, at least about 90 or about 95, *e.g.*, 89, 90, 92 or 93. For example, the naphtha boiling range feed may have a RON from about 80 to about 95, about 85 to about 95 or about 85 to about 90. Motor Octane Number (MON), as measured according to ASTM D2700 and/or ASTM D2885 of the naphtha boiling range feed may be at least about 70, at least about 75, at least about 80 or about 85, *e.g.*, 78, 79, 81, 82 or 83. For example, the naphtha boiling range feed may have a MON from about 70 to about 85, about 75 to about 85 or about 75 to about 80. End point of the naphtha boiling range feed may be in the range of about 200°C to about 240°C, usually about 200°C to about 220°C. T10 (D86) may be determined by fractionation settings, but T50 may be in the range of about 80°C to about 120°C.

[0025] Additionally or alternatively, the naphtha boiling range feed may have a sulfur content, as measured according to ASTM D4294, of at least about 200 ppmw, at least about 300 ppmw, at least about 400 ppmw, at least about 500 ppmw, at least about 600 ppmw, at least about 700 ppmw, at least about 800 ppmw, at least about 900 ppmw, or about 1000 ppmw. The naphtha boiling range feed may have a sulfur content, as measured according to ASTM D4294, of about 200 ppmw to about 1000 ppmw, about 300 ppmw to about 1000 ppmw, about 500 ppmw to about 1000 ppmw, about 500 ppmw to about 900 ppmw, or about 500 ppmw to about 800 ppmw.

[0026] In a particular embodiment, the naphtha boiling range feed may have one or more of the following:

(i) an API gravity of at least about 50 as measured according to ASTM D4052

(ii) a Bromine number of about 50 to about 75 as measured according to ASTM D1159; and

(iii) a sulfur content of at least about 300 ppmw as measured according to ASTM D4294.

In certain aspects, the naphtha boiling range feed may have two of (i)–(iii) (*e.g.*, (i) and (ii), (i) and (iii), (ii) and (iii)) or all three of (i)–(iii).

[0027] Silicon in the naphtha boiling range feed may be primarily present in the FCC naphtha, the straight run naphtha or a combination thereof. For example, the FCC naphtha, the straight run naphtha, or a combination thereof may comprise at least about 50 wt%, at least about 60 wt%, comprise at least about 70 wt%, at least about 80 wt%, comprise at least about 90 wt%, at least about 95wt% or about 100 wt% of the silicon present in the naphtha boiling range feed (based on the total weight of the naphtha boiling range feed). Additionally or alternatively, the FCC naphtha, the straight run naphtha, or a combination thereof may comprise about 50 wt% to about 100 wt%, about 70 wt% to about 100 wt%, about 90 wt% to about 100 wt% or about 95 wt% to about 100 wt% of the silicon present in the naphtha boiling range feed.

[0028] Further, the FCC naphtha, the straight run naphtha, or a combination thereof may comprise about 0.25 ppmw to about 12 ppmw of silicon, about 0.25 to about 10 ppmw of silicon, about 0.50 ppmw to about 10 ppmw silicon or about 0.5 ppmw to about 5.0 ppmw silicon.

[0029] An exemplary naphtha boiling range feed is shown in Table 1 below.

Table 1

API Gravity		55.3
Bromine Number		65
RON		89.3
MON		78.4
Silicon	ppmw	1
Sulphur	ppmw	600
Distillation D86		
IBP	deg C	42
10 vol %	deg C	63
30 vol %	deg C	84
50 vol %	deg C	111
70 vol %	deg C	143
90 vol %	deg C	179
95 vol %	deg C	191
FBP vol %	deg C	205

II.B. Silicon Trap

[0030] As discussed herein, during hydroprocessing, such as hydrodesulfurization processes, silicon (Si) may poison catalysts by bonding with the aluminum carrier and other acidic sites forming silica (SiO_2). The silicon may block the pore system of the catalyst and therefore, access to the active sites, reducing both the activity of the catalyst and its ability to absorb other poisons such as arsenic. The reactions during hydrodesulfurization may be quick and diffusion limited so smaller catalysts may absorb more silicon because their pore system is more accessible. Thus, it has been found that a silicon trap, *e.g.*, comprising inert alumina, should have a larger surface area because silicon species from the silicone additives can form a mono-layer on the catalyst surface; therefore, higher surface area catalysts can have higher silicon absorption capacities. The surface area of the silicon can be determined, for example, using nitrogen adsorption-desorption isotherm techniques within the expertise of one of skill in the art, such as the BET (Brunauer Emmet Teller) method. As used herein, and unless otherwise specified, "surface area" refers to the microporous surface area as determined by the BET method.

[0031] In various aspects, the silicon trap may have surface area of at least about 250 m^2/g, at least about 300 m^2/g, at least about 350 m^2/g or about 400 m^2/g. Additionally or alternatively, the silicon trap may have surface area of about 250 m^2/g to about 400 m^2/g, about 300 m^2/g to about 400 m^2/g, or 350 m^2/g to about 400 m^2/g. While the pore diameter of the alumina may have a role in the silicon retention as a result of limited diffusion, the diffusion limits of larger pores may be relaxed relative to smaller pores, so increasing silicon pickup. Pore diameter may not have a strong impact on silicon capacity, but may typically range from about 70 to about 120 Å (about 7 to about 12 nm).

[0032] Additionally, catalyst particle size can impact silicon removal. Small catalyst particles, *e.g.*, having an average particle size diameter of less than about 1/16 inch (about 1.6m), preferably not more than about 1/20 inch (about 1.25 mm) may be preferred to maximize silicon pickup as silicon removal may become diffusion limited when using larger size catalyst. Table 2 below illustrates the extent of silicon pickup which can be achieved with various alumina trap materials. In Table 2, "SiO_2, wt% fresh" corresponds to the weight of silicon dioxide pickup on the trap, and "Si, lb/ft^3" corresponds to the weight of silicon absorbed by the silicon trap per ft^3 of silicon trap at normal loading density.

Table 2: Silicon Capacities of Aluminas

Size	1/20" Quadrilobe (Quad)	1/20" Trilobe (Tri)	1/20" Quad	1/10" Tri
Pore Diam, Å	116	108	73	86
Surface Area (SA), m^2/g*	250	227	284	242
Density, lb/ft^3	34.3	40.0	41.8	50.5
SiO_2, wt% Fresh	24.1	21.0	17.4	13.6
Si, lb/ft^3 Fresh	3.9	3.9	3.4	3.2
Est. Si Pickup, lb/ft^3 Fresh	3.4	3.6	4.9	4.8

*The SA specification ranges are typically in ± 10 to 15%.

[0033] While silicon trap materials incorporating nickel and cobalt may be recommended for use in a hydrotreating application, use of nickel and cobalt may not be favored in the present process for the following reasons. In the processes described herein, the naphtha boiling range feed may be passed through the silicon trap bed in the presence of hydrogen and any catalytically active metals present on the alumina base may catalyze olefin hydrogenation reactions which are not desired since an objective of the olefin-retentive desulfurization process is to retain olefin octane values to the extent possible consistent with the desired degree of desulfurization. In addition, metals on the trap material may inhibit silicon absorption because active metals (*e.g.*, Co, Ni, Mo) bond with the alumina and reduce the surface area available for bonding with the silicon. The concentration of base metals with hydrogenation activity should be low enough to minimize olefin saturation that can result in an increased octane loss. The metal loadings for common active base metals for this type of silicon trap should be a Group 8, 9, and/or 10 (*e.g.*, nickel, cobalt, ruthenium) content of less than 1.0 about wt% of the finished silicon trap material and a Group 6 (*e.g.*, molybdenum) content of less than about 5.0 wt% of the finished silicon trap material.

[0034] In one particular embodiment, the silicon trap comprising inert alumina may have: a surface area of at least about 250 m^2/g; a particle size less than about 1.6 mm; and a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals (*e.g.*, nickel, cobalt, ruthenium) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum).

[0035] The silicon trap may be loaded at the top bed or initial bed in a hydrodesulfurization (HDS) reactor and operated at the temperature appropriate to the HDS catalyst, as described below. Space velocity can be relatively high since the silicon/alumina reaction is fast, enabling guard bed volume to be limited. Liquid hourly space velocities (LHSV) of 5 hr^{-1} or higher, e.g. 6 hr^{-1} LHSV are suitable.

[0036] Silicon-contaminated guard bed catalysts usually cannot be regenerated. The silicon on the catalyst will turn into glass (SiO_2) during regeneration coating the catalyst particle and blocking the pore system and active sites. Since the silicon deposits at the top of the guard bed first, catalyst from the bottom beds may be regenerated. If arsenic or other poisons are present in the feed, it is preferred that the dominant poison should be removed first. Arsenic traps may be located in the DIOS reactor or in the desulfurization reactor.

II.C. Naphtha Diolefins

[0037] In addition to silicon-containing fragments, FCC naphthas typically have a relatively high level of diolefins, including conjugated diolefins which adversely affect hydrodesulfurization catalysts by polymerizing at bed temperatures and plugging the bed. A diolefin saturation (DIOS) reactor may precede the hydrodesulfurization reactor to stabilize the feed. Diolefin saturation of is a fast reaction and can therefore be carried out at high LHSVs and at low temperatures. Saturation of the troublesome conjugated diolefins can be carried out with the DIOS unit operated at a relatively low temperature in the presence of hydrogen. Using a Group VI/VIII catalyst such as Ni/Mo, Co/Mo at a temperature of about 125-175C, preferably about 140-160C; the exotherm across the DIOS catalyst bed in usually quite low, no more than 10C or less. Pressure is typically about 20 Barg with a space velocity of about 3-4, normally about 4 hr^{-1} LHSV.

II.D. Naphtha Hydrodesulfurization

[0038] The hydrodesulfurization (HDS) of the naphtha boiling range effluent may be carried out in a process in which sulfur is hydrogenatively removed while retaining olefins to the extent feasible. The HDS conditions required to produce a hydrotreated naphtha stream which contains non-mercaptan sulfur at a level below mogas specification as well as significant amounts of mercaptan sulfur will vary as a function of the concentration of sulfur and types of organic sulfur in the naphtha boiling range effluent to the HDS unit. Generally, the processing conditions may fall within the following ranges: about 250°C to about 325°C (about 475–620°F); about 1000 KPag to about 3500 kPag (about 150–500 psig) total pressure; about 600 kPa to about 2500 kPa (about 90–360 psig) hydrogen partial pressure, about 200 Nm^3/m^3 to about 300 Nm^3/m^3 hydrogen treat gas rate, and about 1 hr^{-1} LHSV to about 10 hr^{-1} LHSV. The olefin-retentive selective catalytic naphtha hydrotreating process available under license from ExxonMobil Research and Engineering Company as the SCANfining™ process may be preferred for this purpose as it optimizes desulfurization and denitrogenation while retaining olefins for gasoline octane. SCANfining™ is described in National Petroleum Refiners Association Paper AM-99-31 titled "Selective Cat Naphtha Hydrofining with Minimal Octane Loss." Other suitable olefin retentive selective catalytic naphtha hydrodesulfurization processes contemplated here are as those described in US Patent Nos. 5,853,570; 5,906,730; 4,243,519; 4,131,537; 5,985,136 and 6,013,598 (to which reference is made for descriptions of such processes).

[0039] Typical SCANfining™ conditions may include one and two stage processes for hydrodesulfurizing a naphtha boiling range effluent as described herein. The hydrodesulfurization may comprise reacting the naphtha boiling range effluent in a first reaction stage under hydrodesulfurization conditions including contacting the naphtha boiling range effluent with a catalyst. The catalyst may comprise about 1 wt% to about 10 wt% MoO_3 and about 0.1 wt% to about 5 wt% CoO. Additionally or alternatively, the catalyst may have one or more of the following:

(i) a Co/Mo atomic ratio of about 0.1 to about 1.0;

(ii) a median pore diameter of about 6 nm to about 20 nm;

(iii) a MoO_3 surface concentration in g MoO_3/m^2 of about 0.5×10^{-4} to about 3×10^{-4}; and

(iv) an average particle size diameter of less than about 2.0 mm.

[0040] Additionally or alternatively, the catalyst may have two of (i)–(iv) (*e.g.*, (i) and (ii), (i) and (iii), (i) and (iv), (ii) and (iii), (ii) and (iv), (iii) and (iv)), three of (i)–(iv) (*e.g.*, (i), (ii), and (iii); (i), (iii) and (iv); (i), (ii) and (iv); (ii), (iii) and (iv)) or all of (i)–(iv).

[0041] The first stage reaction product may then be optionally passed to a second stage, also operated under hydrodesulfurization conditions as described herein, wherein, the first stage reaction product may contact a catalyst comprised of at least one Group 8, 9 or 10 metal, such as cobalt and nickel, and at least one Group 6 metal, such as molybdenum and tungsten, preferably molybdenum, on an inorganic oxide support material such as alumina. A non-limiting example of a suitable catalyst is the Albemarle Catalyst RT-235.

[0042] In certain embodiments, a two-stage hydrodesulfurization process is provided. For example, the naphtha boiling range effluent may be contacted with hydrogen and a hydrotreating catalyst in a first vapor reaction stage to remove at least about 70 wt% of sulfur present in the naphtha boiling range effluent to produce a first stage effluent. The first stage effluent may comprise a mixture of reduced sulfur naphtha and H_2S. The process may further comprise separating the reduced sulfur naphtha and H_2S, *e.g.*, by cooling the mixture of reduced sulfur naphtha and H_2S to condense the reduced sulfur naphtha vapor to a liquid containing dissolved H_2S, which may then be separated from the H_2S containing gas. In the second stage, the reduced sulfur naphtha may be contacted with hydrogen and a hydrodesulfurization catalyst in a second vapor reaction stage having a temperature at least about 10°C (about 20°F) greater than in the first vapor reaction stage and a space velocity at least about 1.5 times greater than in the first vapor reaction stage to remove at least about 80 wt% of remaining sulfur from the reduced sulfur naphtha to form a desulfurized naphtha product. The desulfurized naphtha product, if in vapor form, may then be cooled to condense and separate naphtha from the H_2S to form a desulfurized naphtha product liquid. The desulfurized naphtha product (liquid) may contain less than about 5.0 wt% of the amount of the sulfur present in the naphtha boiling range effluent but retaining at least 40 vol% of the olefin content of the naphtha boiling range effluent. In various aspects, the naphtha boiling range effluent may comprise the same amount of sulfur as in the naphtha boiling range feed as described herein (*e.g.*, at least about 300 wppm, at least about 400 wppm, *etc.*). In particular, the naphtha boiling range effluent may comprise at least about 300 wppm sulfur.

[0043] In the two-stage process, the hydtrotreating catalyst and the hydrodesulfurization catalyst in both stages may comprise Co and Mo on a support and present in an amount of less than a total of 12 wt% calculated as the respective metal oxides CoO and MoO_3 with a Co to Mo atomic ratio from 0.1 to 1.0. Reaction conditions in each stage may range from about 230°C to about 400°C (about 450–750°F), a pressure of from about 400 kPag to about 34000 kPag (about 60–600 psig), a treat gas ratio of from about 1000 scf/b to about 4000 scf/b and a space velocity of from about 1 v/v/hr to about 10 v/v/hr. Under these conditions, the percent desulfurization in the second vapor reaction stage may be at least about 80%, at least about 90% or at least about 95%/. Space velocity in the second vapor reaction stage be greater than that in the first vapor reaction stage and can range up to 6 hr^{-1} LHSV. Table 3 below shows an example of typical SCANfining™ reactor operating conditions.

Table 3

Reactor Outlet Temperature	°C	273
Bed Average Temperature	°C	261
Total Exotherm	°C	24
Reactor Inlet Pressure	barg	19.0
Treat Gas Rate	Nm^3/m^3	253
Treat Gas Purity	vol % H_2	94.0
Desulfurization	% HDS	83.0
Olefin Saturation	% OSAT	15.4

[0044] During hydrogenative sulfur removal processes, such as SCANfining™, the organic sulfur may be converted to inorganic form, such as hydrogen sulfide (H_2S), but some mercaptans may remain in the product stream. A subsequent mercaptan decomposition stage may be included to reduce the content of mercaptan sulfur in the final product stream. Suitable mercaptan removal processes are described in US Patent Publication Nos. 2007/114156 and 2014/174982.

[0045] The sulfur content of the desulfurized product may be substantially reduced but it may not comply itself with finished gasoline requirements. However, the desulfurized product may be satisfactory as a component in the gasoline pool when blended with other gasoline range fractions such as straight run naphtha, alkylate, reformate, *etc.* to make a blend for ethanol at the product terminal. An example of a desulfurized product's quality is shown in Table 4 below.

Table 4 : Desulfurized Product Quality

Total Sulfur	ppmw	50
Bromine No.	cg/g	51.6
Olefins	LV%	30
API Gravity	°API	60.2
RON		90
MON		82

III. Further Embodiments

[0046] The invention can additionally or alternatively include one or more of the following embodiments.

[0047] Embodiment 1. A process for desulfurizing a naphtha boiling range feed comprising: contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha, or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent; and hydrodesulfurizing at least a portion the naphtha boiling range effluent, optionally, wherein the inert alumina has one or more of:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and

a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum).

[0048] Embodiment 2. A process for removing silicon from a naphtha boiling range feed comprising: contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent, wherein the inert alumina has:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and

a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum); and optionally, hydrodesulfurizing at least a portion of the naphtha boiling range effluent.

[0049] Embodiment 3. The process of embodiment 1 or 2, wherein the naphtha boiling range feed does not include delayed coker naphtha.

[0050] Embodiment 4. A process for desulfurizing a naphtha boiling range feed comprising: contacting the naphtha boiling range feed comprising fluid catalytic cracker naphtha, straight run naphtha, delayed coker naphtha or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent; and hydrodesulfurizing at least a portion of the naphtha boiling range effluent, optionally, wherein the inert alumina has one or more of:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum).

[0051] Embodiment 5. The process of any one of the previous embodiments, wherein the naphtha boiling range feed has one or more of the following:

(i) an API gravity of at least about 50 as measured according to ASTM D4052;

(ii) a Bromine number of about 50 to about 75 as measured according to ASTM D1159; and

(iii) a sulfur content of at least about 300 ppmw as measured according to ASTM D4294.

[0052] Embodiment 6. The process of any one of the previous embodiments, wherein the fluid catalytic cracker naphtha, the straight run naphtha, or the combination thereof comprises at least about 90 wt%, preferably about 100 wt% of the silicon present in the naphtha boiling range feed.

[0053] Embodiment 7. The process of any one of the previous embodiments, wherein the fluid catalytic cracker naphtha, the straight run naphtha, or the combination thereof comprises about 0.25 ppmw to about 10.0 ppmw of silicon.

[0054] Embodiment 8. The process of any one of the previous embodiments, wherein the hydrodesulfurization is carried out at a temperature of about 250°C to about 325°C, a total system pressure of about 1000 kPag to about 3500 kPag, a hydrogen partial pressure of about 600kPa to about 2500 kPa and a liquid hourly space velocity (LHSV) of about 1.0 hr^{-1} to about 10 hr^{-1}.

[0055] Embodiment 9. The process of any one of the previous embodiments, wherein the hydrodesulfurization comprises contacting the naphtha boiling range effluent with a catalyst comprising: about 1.0 wt% to about 10 wt% MoO_3; and about 0.1 to 5 wt. % CoO; wherein the catalyst has one or more of the following:

(i) a Co/Mo atomic ratio of about 0.1 to about 1.0,

(ii) a median pore diameter of about 6 nm to about 20 nm;

(iii) a MoO_3 surface concentration of about 0.5×10^{-4} g MoO_3/m^2 to about 3×10^{-4} g MoO_3/m^2; and

(iv) an average particle size diameter of less than about 2.0 mm.

[0056] Embodiment 10. The process of any one of the previous embodiments, wherein the hydrodesulfurization is performed in a two stage process comprising: (i) contacting the naphtha boiling range effluent with hydrogen and a hydrotreating catalyst in a first vapor reaction stage to remove at least about 70 wt% of sulfur present in the naphtha boiling range effluent to produce a first stage effluent comprising a mixture of reduced sulfur naphtha and H_2S; and separating the reduced sulfur naphtha and H_2S; and (ii) contacting the reduced sulfur naphtha and hydrogen with a hydrodesulfurization catalyst in a second vapor reaction stage having a temperature at least about

10°C greater than in the first vapor reaction stage and a space velocity at least about 1.5 times greater than in the first vapor reaction stage to remove at least about 80 wt% of remaining sulfur from the reduced sulfur naphtha to form a desulfurized naphtha product.

[0057] Embodiment 11. The process of any one of the previous embodiments, wherein the naphtha boiling range effluent comprises at least about 300 wppm sulfur.

[0058] Embodiment 12. The process of embodiment 9 or 10, wherein the desulfurized naphtha product comprises less than about 5.0 wt% of the amount of sulfur present in the naphtha boiling range effluent but retains at least 40 vol% of the olefin content of the naphtha boiling range effluent.

[0059] Embodiment 13. The process of any one of embodiments 9 to 11, wherein both the hydrotreating catalyst and the hydrodesulfurization catalyst comprise Co and Mo on a support in an amount of less than a total of about 12 wt% calculated as the respective metal oxides CoO and MoO_3 with a Co/Mo atomic ratio from 0.1 to 1.0.

[0060] Embodiment 14. The process of any one of embodiments 9 to 12, wherein the reaction conditions in each stage have a temperature from about 230°C to about 400°C, a pressure from about 400 KPag to about 34000 kPag, and a space velocity from about 1 v/v/hr to about 10 v/v/hr, wherein a space velocity in the second vapor reaction stage is greater than that in the first vapor reaction stage.

[0061] Embodiment 15. The process of any one of embodiments 9 to 13, wherein the percent desulfurization in the second vapor reaction stage is at least about 90%.

CLAIMS:

1. A process for desulfurizing a naphtha boiling range feed comprising:

contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha, or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent; and

hydrodesulfurizing at least a portion the naphtha boiling range effluent, optionally, wherein the inert alumina has one or more of:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and

a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum).

2. A process for removing silicon from a naphtha boiling range feed comprising: contacting the naphtha boiling range feed consisting essentially of fluid catalytic cracker naphtha, straight run naphtha or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent, wherein the inert alumina has:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and

a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum);

and optionally, hydrodesulfurizing at least a portion of the naphtha boiling range effluent.

3. The process of claim 1 or 2, wherein the naphtha boiling range feed does not include delayed coker naphtha.

4. A process for desulfurizing a naphtha boiling range feed comprising:

contacting the naphtha boiling range feed comprising fluid catalytic cracker naphtha, straight run naphtha, delayed coker naphtha or a combination thereof with a silicon trap comprising inert alumina to remove silicon from the naphtha boiling range feed to form a naphtha boiling range effluent; and

hydrodesulfurizing at least a portion of the naphtha boiling range effluent, optionally, wherein the inert alumina has one or more of:

a surface area of at least about 250 m^2/g, preferably at least about 300 m^2/g;

an average particle diameter of less than about 1.6 mm; and a metal content of not more than about 1.0 wt% Group 8, 9 or 10 metals (*e.g.*, nickel, cobalt) and not more than about 5.0 wt% Group 6 metals (*e.g.*, molybdenum).

5. The process of any one of the previous claims, wherein the naphtha boiling range feed has one or more of the following:

(iv) an API gravity of at least about 50 as measured according to ASTM D4052;

(v) a Bromine number of about 50 to about 75 as measured according to ASTM D1159; and

(vi) a sulfur content of at least about 300 ppmw as measured according to ASTM D4294.

6. The process of any one of the previous claims, wherein the fluid catalytic cracker naphtha, the straight run naphtha, or the combination thereof comprises at least about 90 wt%, preferably about 100 wt% of the silicon present in the naphtha boiling range feed.

7. The process of any one of the previous claims, wherein the fluid catalytic cracker naphtha, the straight run naphtha, or the combination thereof comprises about 0.25 ppmw to about 10.0 ppmw of silicon.

8. The process of any one of the previous claims, wherein the hydrodesulfurization is carried out at a temperature of about 250°C to about 325°C, a total system pressure of about 1000 kPag to about 3500 kPag, a hydrogen partial pressure of about 600kPa to about 2500 kPa and a liquid hourly space velocity (LHSV) of about 1.0 hr^{-1} to about 10 hr^{-1}.

9. The process of any one of the previous claims, wherein the hydrodesulfurization comprises contacting the naphtha boiling range effluent with a catalyst comprising: about 1.0 wt% to about 10 wt% MoO_3; and about 0.1 to 5 wt. % CoO; wherein the catalyst has one or more of the following:

(v) a Co/Mo atomic ratio of about 0.1 to about 1.0,

(vi) a median pore diameter of about 6 nm to about 20 nm;

(vii) a MoO_3 surface concentration of about 0.5×10^{-4} g MoO_3/m^2 to about 3×10^{-4} g MoO_3/m^2; and

(viii) an average particle size diameter of less than about 2.0 mm.

10. The process of any one of the previous claims, wherein the hydrodesulfurization is performed in a two stage process comprising: (i) contacting the naphtha boiling range effluent with hydrogen and a hydrotreating catalyst in a first vapor reaction stage to remove at least about 70 wt% of sulfur present in the naphtha boiling range effluent to produce a first stage effluent comprising a mixture of reduced sulfur naphtha and H_2S; and separating the reduced sulfur naphtha and H_2S; and (ii) contacting the reduced sulfur naphtha and hydrogen with a hydrodesulfurization catalyst in a second vapor reaction stage having a temperature at least about 10°C greater than in

the first vapor reaction stage and a space velocity at least about 1.5 times greater than in the first vapor reaction stage to remove at least about 80 wt% of remaining sulfur from the reduced sulfur naphtha to form a desulfurized naphtha product.

11. The process of any one of the previous claims, wherein the naphtha boiling range effluent comprises at least about 300 wppm sulfur.

12. The process of claim 9 or 10, wherein the desulfurized naphtha product comprises less than about 5.0 wt% of the amount of sulfur present in the naphtha boiling range effluent but retains at least 40 vol% of the olefin content of the naphtha boiling range effluent.

13. The process of any one of claims 9 to 11, wherein both the hydrotreating catalyst and the hydrodesulfurization catalyst comprise Co and Mo on a support in an amount of less than a total of about 12 wt% calculated as the respective metal oxides CoO and MoO_3 with a Co/Mo atomic ratio from 0.1 to 1.0.

14. The process of any one of claims 9 to 12, wherein the reaction conditions in each stage have a temperature from about 230°C to about 400°C, a pressure from about 400 KPag to about 34000 kPag, and a space velocity from about 1 v/v/hr to about 10 v/v/hr, wherein a space velocity in the second vapor reaction stage is greater than that in the first vapor reaction stage.

15. The process of any one of claims 9 to 13, wherein the percent desulfurization in the second vapor reaction stage is at least about 90%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/015129

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G25/00 C10G67/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/046881 A1 (SHIH STUART S [US] ET AL) 18 February 2016 (2016-02-18) cited in the application claims 1, 5-12 paragraphs [0010], [0011], [0019] - [0021] -----	1-15
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 28 March 2018	Date of mailing of the international search report 10/04/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pardo Torre, J

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/015129

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ATTILA LENGYEL ET AL: "Catalytic Co-Processing of delayed coker light naphtha with other refinery gasoline streams", PERIODICA POLYTECHNICA. CHEMICAL ENGINEERING, vol. 53, no. 1, 1 January 2009 (2009-01-01), pages 3-7, XP055463470, HU ISSN: 0324-5853, DOI: 10.3311/pp.ch.2009-1.01 1.Introduction -----	1-15
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