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(54) **DISTILLATE DESULFURIZATION PROCESS**

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(57) **ABSTRACT**

A process is disclosed for the ultradeep desulfurization of a sulfur-containing distillate feedstock.

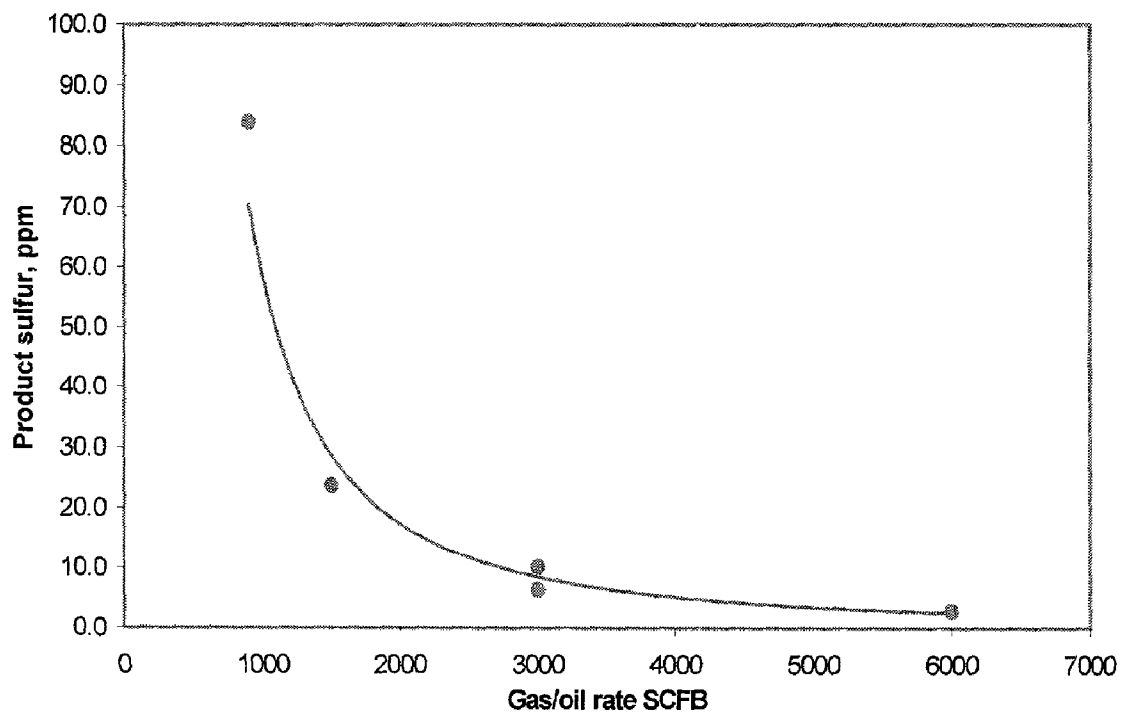
The hydrodesulfurization process conditions employed in the process of the invention include a hydrogen circulation rate of at least five times the molar consumption rate of hydrogen and a feedstock vaporization of at least 30 mole percent.

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FIG. 1

Desulfurization response to gas rate at 812psi, 650F, 2 LHSV



DISTILLATE DESULFURIZATION PROCESS

BACKGROUND OF THE INVENTION

[0001] The desire to provide a cleaner environment has resulted in substantial regulation of fuels and in particular the sulfur contents of fuels. Sulfur in diesel fuel can result in the catalytic oxidation of SO_2 to SO_3 in diesel engine exhaust gases where a catalytic emission control device is used. This SO_3 combines with water to form sulfuric acid emitted as a mist particulate. Further, sulfur containing exhaust gases can result in exhaust gas emission catalyst poisoning with respect to NOx conversion activity.

[0002] The US Environmental Protection Agency is targeting a level of sulfur less than 15 ppm in 2006 for on-road diesel. The European Union specification will be less than 50 ppm in 2005. Further the World Wide Fuels Charter as supported by all global automobile manufacturers proposes even more stringent sulfur requirements of 5 to 10 ppm for the Category IV fuels for "advanced" countries. In order to comply with these regulations for ultra-low sulfur content fuels, refiners will have to make fuels having even lower sulfur levels at the refinery gate. Thus refiners are faced with the challenge of reducing the sulfur levels in fuels and in particular diesel fuel within the timeframes prescribed by the regulatory authorities.

[0003] A hydrodesulfurization process is often employed to reduce the concentration of organosulfur compounds in hydrocarbons. The hydrodesulfurization is carried out by contacting a hydrocarbon feedstock with hydrogen at elevated temperatures and pressures in the presence of a hydrodesulfurization catalyst in order to convert the organosulfur compounds to hydrogen sulfide.

[0004] In conventional hydrodesulfurization processes those skilled in the art typically will operate the reaction zone with a hydrogen circulation rate of approximately three times the chemical hydrogen consumption rate on a molar basis. This circulation rate is maintained in order to maintain the hydrogen partial pressure and avoid excessive increase in the concentration of hydrogen sulfide. Generally, the heavier the feedstock the greater the chemical hydrogen consumption rate and hence the desired hydrogen circulation rate. Thus for distillate feedstock desulfurization, the circulation rate would generally be in the range of about 600 to about 2000 standard cubic feet per barrel of feedstock ("SCFB"). Above this range the hydrogen partial pressure and hydrogen sulfide partial pressure tend to level off so there is no incentive for increasing the circulation rate beyond about three four times the hydrogen consumption rate. In fact, there are considerable economic disincentives to increasing the hydrogen circulation rate because of the increased utility costs and capital costs associated with the compression and circulation of the hydrogen and the increased pressure drop associated with a higher circulation rate.

[0005] In order to reach these desirable low levels of sulfur, the prior art discloses many hydrodesulfurization processes including many multi-step processes. Typical reasons for using multi-step processes are that such processes permit the separation of liquid and vapor between stages, the use of a sulfur sensitive catalyst in a second stage, the improvement of color of diesel fuel with special second stage reaction conditions, the use of alternative reactor

designs in the different stages, the hydrogenation of aromatics, the processing of heavier feedstocks, and the preparation of various specialty products other than low-sulfur fuel.

[0006] In this connection, U.S. Pat. No. 6,171,477 B1 (Morel et al.) discloses a multi-step process that includes a desulfurization step with a heavy hydrocarbon feedstock having an initial boiling point of at least 360°C . and a final boiling point of at least 500°C . wherein the hydrogen circulation step is about 100 to about 5000 normal cubic meters (Nm^3) per cubic meter (m^3) of liquid charge (594 to 29,700 SCFB) with a most preferable charge of about 300 to about $500\text{ Nm}^3/\text{m}^3$ (1782 to 2970 SCFB). This feedstock is a much heavier feedstock than the distillates used for diesel production, and consumes much more hydrogen and therefore requires much higher hydrogen circulation to supply hydrogen for consumption, to maintain hydrogen partial pressure, and to control buildup of hydrogen sulfide.

[0007] U.S. Pat. No. 5,403,470 (Kokayeff et al.) discloses a two-stage process for improving the color of a diesel feedstock wherein the first hydrotreating stage is carried out to decrease the organosulfur content to less than 800 ppmw with a gas recycle rate of 400 to about 4000 standard cubic feet per barrel of feedstock. This process is a two-stage process in which the purpose of the second stage is to improve product color.

[0008] U.S. Pat. No. 5,316,658 (Ushio et al.) discloses a two-stage process for the production of low sulfur diesel gas oil having a Saybolt color number of -10 or higher. Specifically the hydrodesulfurization is carried out in the first stage at a hydrogen to oil ratio of 200 to about 5000 scf/bbl and more preferably 500 to 2000 scf/bbl. The purpose of the second stage is to improve the product color.

[0009] U.S. Pat. No. 5,068,025 (Bhan) discloses a two-stage process for the concomitant hydrogenation of aromatics and sulfur bearing hydrocarbons in a diesel boiling range hydrocarbon feedstock. The subject process discloses that the hydrogen feed rate will typically be 100 to about 5000 scf/bbl.

[0010] U.S. Pat. No. 4,431,526 (Simpson et al.) discloses a two-stage process for hydroprocessing heavier feedstocks such as "hydrocarbon containing oils" including all liquid and liquid/vapor hydrocarbon mixtures such as crude petroleum oils and synthetic crudes, e.g. top crudes, vacuum and atmospheric residual fractions, heavy vacuum distillates, shale oils, oils from bituminous sands, coal compositions which contain sulfur and contaminant metal. Due to the heavy nature of these feedstocks, the hydrogen circulation rate is disclosed to be in the range of about 1000 to about 15,000 scf/bbl.

[0011] U.S. Pat. No. 5,114,562 (Haun et al.) discloses another two-stage process with inter-stage stripping wherein a middle distillate petroleum stream is hydrotreated to produce a low sulfur and low aromatic product. The second stage employs a sulfur sensitive noble metal catalyst to saturate the aromatics which saturation consumes hydrogen. The circulation rate in the first reaction zone is disclosed as ranging from 400 for light naphthas to 20,000 scf/bbl for cycle oils and preferably between 1,500 and 5,000 scf/bbl. The subject patent indicates that the average molecular weight of the feedstream is reduced by the virtue of the production of gasoline and LPG.

[0012] U.S. Pat. No. 3,147,210 (Hass et al.) discloses yet another two-stage hydrogenation process with inter-stage stripping, using a sulfur-sensitive noble metal catalyst in the second stage with a goal of high aromatics saturation. The hydrogen circulation rate is disclosed as ranging from 200 to 12,000 scf/bbl, preferably 1,000 to 8,000 scf/bbl for the hydrofining stage. The example discloses a circulate rate of 700 s.c.f./b for the hydrofining stage.

[0013] U.S. Pat. No. 6,251,262 B1 (Hatanaka et al.) discloses a three-stage hydrodesulfurization process for diesel gas oil wherein the hydrogen to oil ratio is about 1000 to about 5000 scf/bbl wherein a product having a sulfur content of 0.005 wt. % is recovered.

[0014] U.S. Pat. No. 5,110,444 (Haun et al.) discloses another three-stage process. This process uses three stages with counter current gas/liquid flow, inter-stage stripping, and noble metal catalysts in 2nd and 3rd stages. The patent refers to gas rates as high as 20,000 SCFB, with preferred range of 1,500 to 5,000 SCFB. The use of higher gas rates in the 2nd and/or 3rd stages, accommodates the H₂ consumption engendered by aromatics saturation catalyzed by the noble metal catalysts.

[0015] U.S. Pat. No. 6,251,263 B1 (Hatanaka et al.) discloses a three-reaction zone hydrogenation process that uses specific catalysts in specific ratios using hydrogen circulation rates of 1000 to 5000 scf/bbl. While the Patentees maintain they can reach deep desulfurization level of 0.0001 wt % (1 ppmw), the examples only disclose higher levels with Example 3 showing an effluent having 30 ppmw where the feedstock was a Middle East straight run gas oil.

[0016] U.K. Patent 1,385,288 discloses a multi-stage process for the simultaneous production of a jet fuel and motor fuel which comprises passing a hydrocarbon oil into a hydrotreating zone and passing the effluent from the hydrotreating zone to a multi-stage hydrocracking zone. The patent discloses a hydrogen circulation rate of 1,000 to 50,000 SCFB. This is a hydrocracking process which cracks heavy feeds into lighter products and in so doing consumes much more hydrogen than a hydrodesulfurization process.

[0017] There is a need to develop a hydrodesulfurization process that achieves the deep desulfurization of distillates to levels wherein the product will have sulfur contents no greater than 50 ppmw, preferably less than 15 ppmw and most preferably less than 10 ppmw. Further inasmuch as refineries are up against aggressive regulatory timetables, there is a need to achieve this deep desulfurization efficaciously and quickly without the use of exotic new catalysts. This desired deep desulfurization will require a process that can convert the highly difficult- to-desulfurize compounds present in the high boiling fraction of a distillate feedstock.

[0018] It has now been discovered that such deep desulfurization of distillate feedstocks can be effected without the use of exotic catalysts by increasing the hydrogen circulation rate to a distillate hydrodesulfurization zone well beyond the levels disclosed and recommended in the prior art while concomitantly increasing the volatilization of the feedstock to a relatively high level.

SUMMARY OF THE INVENTION

[0019] The process of the present invention achieves deep desulfurization of distillate hydrocarbon feedstock to a level

below 50 ppmw sulfur in a conventional hydrodesulfurization process reaction zone in the presence of a conventional hydrodesulfurization catalyst wherein the process is carried out at hydrogen circulation rate of at least 5 times the molar chemical hydrogen consumption rate and wherein the distillate feedstock is vaporized in the reaction zone to at least about 30 mole percent of the total feedstock. In another embodiment, the process of the present invention involves carrying out the hydrodesulfurization process in a multi-stage process wherein at least one stage is carried out at conventional operating conditions including a conventional hydrogen circulation rate and a conventional feedstock vaporization wherein the more reactive sulfur compounds are removed and wherein at least one additional downstream stage is carried out at process conditions that include a hydrogen circulation rate of at least 5 times the chemical hydrogen consumption rate and wherein the distillate feedstock vaporization is at least about 30 mole percent of the total feedstock.

BRIEF DESCRIPTION OF THE DRAWING

[0020] FIG. 1 is a graph showing the relationship between desulfurization as achieved by the hydrodesulfurization process of the present invention versus the desulfurization achieved by a process employing the prior art hydrogen circulation rate and vaporization rate.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0021] The hydrocarbon feedstock suitable for use with the present invention generally comprises a substantial portion of a distillate hydrocarbon feedstock, wherein a "substantial portion" is defined as, for purposes of the present invention, at least 50% of the total feedstock by volume. The distillate hydrocarbon feedstock processed in the present invention consists essentially of any one, several, or all refinery streams boiling in a range from about 150° F. to about 700° F., preferably 300° F. to about 700° F., and more preferably between about 350° F. and about 700° F. at atmospheric pressure. For the purpose of the present invention, the term "consisting essentially of" is defined as at least 95% of the feedstock by volume. The lighter hydrocarbon components in the distillate product are generally more profitably recovered to gasoline and the presence of these lower boiling materials in distillate fuels is often constrained by distillate fuel flash point specifications. Heavier hydrocarbon components boiling above 700° F. are generally more profitably processed as fluidized catalytic cracking process ("FCC") feed and converted to gasoline. The presence of heavy hydrocarbon components in distillate fuels is further constrained by distillate fuel end point specifications.

[0022] The distillate hydrocarbon feedstock can comprise high and low sulfur virgin distillates derived from high- and low-sulfur crudes, coker distillates, catalytic cracker light and heavy catalytic cycle oils, and distillate boiling range products from hydrocracker and resid hydrotreater facilities. Generally, coker distillate and the light and heavy catalytic cycle oils are the most highly aromatic feedstock components, ranging as high as 80% by weight (FIA). The majority of coker distillate and cycle oil aromatics are present as monoaromatics and di-aromatics with a smaller portion present as tri-aromatics. Virgin stocks such as high and low sulfur virgin distillates are lower in aromatics content rang-

ing as high as 20% by weight aromatics (FIA). Generally, the aromatics content of a combined hydrogenation facility feedstock will range from about 5% by weight to about 80% by weight, more typically from about 10% by weight to about 70% by weight, and most typically from about 20% by weight to about 60% by weight. In a distillate hydrodesulfurization facility with limited operating capacity, it is generally preferable (most economical) to process feedstocks in order of highest aromaticity, since catalytic processes often proceed to equilibrium product aromatics concentrations. In this manner, maximum distillate pool dearomatization is generally achieved.

[0023] The distillate hydrocarbon feedstock sulfur concentration is generally a function of the high and low sulfur crude mix, the hydrodesulfurization capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrodesulfurization feedstock components. The higher sulfur distillate feedstock components are generally virgin distillates derived from high sulfur crude, coker distillates, and catalytic cycle oils from fluid catalytic cracking units processing relatively higher sulfur feedstocks. These distillate feedstock components can range as high as 2% by weight elemental sulfur but generally range from about 0.1% by weight to about 0.9% by weight elemental sulfur.

[0024] The distillate hydrocarbon feedstock nitrogen content is also generally a function of the nitrogen content of the crude oil, the hydrodesulfurization capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrodesulfurization feedstock components. The higher nitrogen distillate feedstocks are generally coker distillate and the catalytic cycle oils. These distillate feedstock components typically have total nitrogen concentrations ranging as high as 2,000 ppm, but generally range from about 1 ppm to about 900 ppm.

[0025] The hydrodesulfurization process of the present invention generally begins with a distillate feedstock preheating step. The feedstock is preheated in feed/effluent heat exchangers prior to entering a furnace for final preheating to a targeted reaction zone inlet temperature that will assist in achieving the vaporization rate in accordance with the present invention. The feedstock can be contacted with a hydrogen stream prior to, during, and/or after preheating.

[0026] The hydrogen stream can be pure hydrogen or can be in admixture with diluents such as low-boiling hydrocarbons, carbon monoxide, carbon dioxide, nitrogen, water, sulfur compounds, and the like. The hydrogen stream purity should be at least about 50% by volume hydrogen, preferably at least about 65% by volume hydrogen, and more preferably at least about 75% by volume hydrogen for best results. Hydrogen can be supplied from a hydrogen plant, a catalytic reforming facility, or other hydrogen-producing or hydrogen-recovery processes.

[0027] The reaction zone can consist of one or more fixed bed reactors containing the same or different catalysts. A fixed bed reactor can also comprise a plurality of catalyst beds. The plurality of catalyst beds in a single fixed bed reactor can also comprise the same or different catalysts.

[0028] In another embodiment, the process of the present invention as explained in greater detail below, comprises a multi-stage process having more than one reaction zone.

[0029] Since the hydrodesulfurization reaction is generally exothermic, interstage cooling, consisting of heat transfer devices between catalyst beds in the same reactor shell, can be employed. At least a portion of the heat generated from the hydrodesulfurization process can often be profitably recovered for use in the hydrodesulfurization process. A suitable heat sinks for absorbing such heat provided by the hydrodesulfurization reaction exotherm can and generally includes the feedstock preheat section of the hydrodesulfurization process upstream of the reactor preheat furnace described hereinabove. Where this heat recovery option is not available, cooling of the reaction zone effluent may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream injected directly into the reactors.

[0030] The reaction zone effluent is generally cooled and the effluent stream is directed to a separator device to remove the hydrogen. Some of the recovered hydrogen can be recycled back to the process while some of the hydrogen can be purged to external systems such as plant or refinery fuel. The hydrogen purge rate is often controlled to maintain a minimum hydrogen purity and to remove hydrogen sulfide. Recycled hydrogen is generally compressed, supplemented with "make-up" hydrogen, and reinjected into the process for further hydrodesulfurization. Hydrogen is preferably passed through the reaction zone or zones in a multi-stage process, in a co-current fashion.

[0031] The separator device liquid effluent can then be processed in a stripper device where light hydrocarbons can be removed and directed to more appropriate hydrocarbon pools. The stripper liquid effluent product is then generally conveyed to blending facilities for production of finished distillate products.

[0032] It is an essential feature of the present invention that the hydrogen circulation rate be at least 5 times the chemical molar hydrogen consumption rate. It is preferable that the rate be at least 10 times the chemical molar hydrogen consumption rate and most preferably at least 20 times the chemical molar hydrogen consumption rate. For a typical distillate feedstock having a hydrogen consumption rate of 600 SCFB, these hydrogen circulation values correspond to 3,000 SCFB, 6,000 SCFB, and 12,000 SCFB, respectively.

[0033] It is another essential feature of the present invention that the percentage feedstock vaporization be at least 30 mole %, preferably at least 40 mole % and most preferably at least 50 mole %. Generally, the feedstock vaporization is a complex function of the feedstock boiling range and composition, reactor temperature, reactor pressure, and hydrogen circulation rate. Those skilled in the art can readily calculate the percentage vaporization or employ one of the commercially available software programs such as Hysis or PRO-II to compute the percentage vaporization. When the temperature, pressure, and circulation rate are predetermined refiners operate the hydrodesulfurization process at the percentage vaporization determined by the forgoing set conditions. Percentage vaporization in the hydrodesulfurization reaction zone is a dependent variable that the refiner generally does not monitor. In the process of the present invention, the hydrogen circulation rate is used to manipulate the percentage vaporization and to set the vaporization at a desired level in accordance with the present invention.

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