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(54) **DISTILLATE DESULFURIZATION PROCESS**

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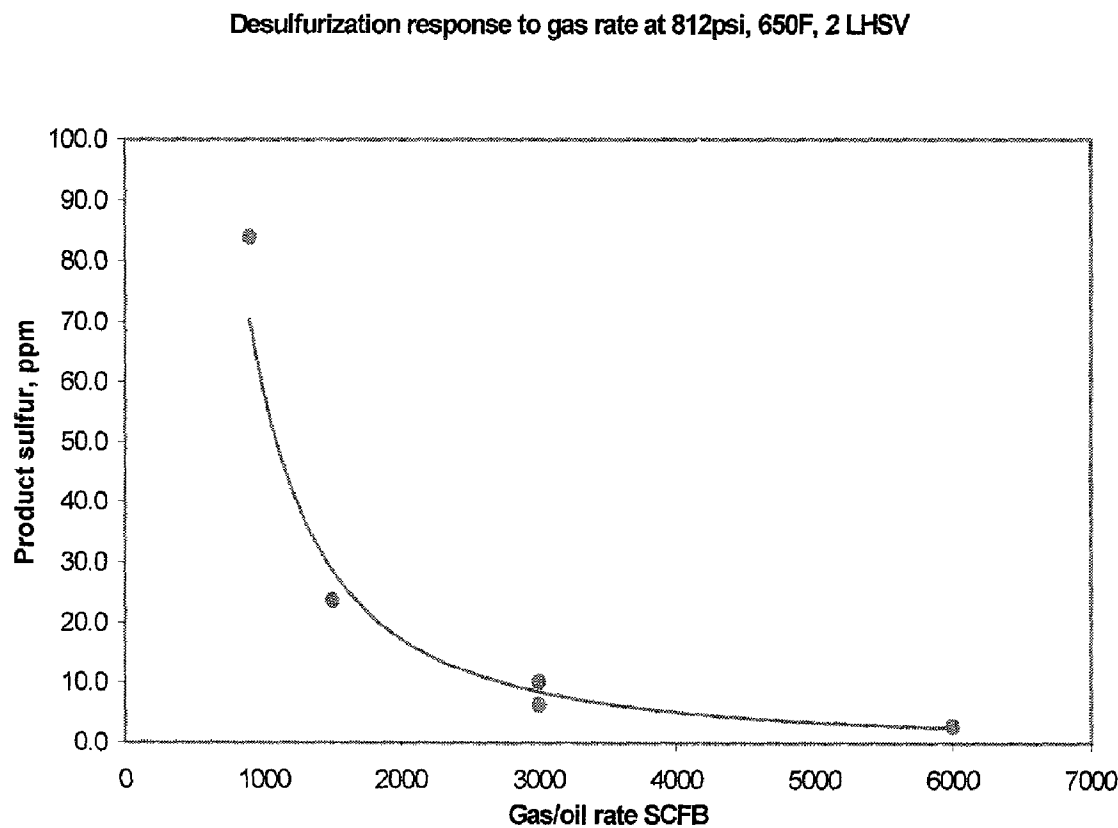
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(57) **ABSTRACT**

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.

FIG. 1



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 NO_x 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 refiners 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 sink 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.

The percentage vaporization should be set at the high levels of the present invention in order to concentrate the sulfur reactants in the liquid phase and thereby accelerate their reaction.

[0034] The hydrogen circulation rates required by the process of the present invention can be achieved by adding more compressors, or by running the compressors at greater severity, or by feeding less feedstock to increase the gas-to-oil ratio.

[0035] In conventional distillate desulfurization, at typical operating conditions, the mole percent vaporization of feed is about 15% at about 1000 SCFB gas/oil circulation rate and about 25% at about 2000 SCFB gas/oil circulation rate. In accordance with this invention, the feed vaporization is increased to at least 30 mole % by increasing gas/oil circulation rates to about 5000 SCFB, or higher for a typical feedstock. Essentially, full vaporization of the feed typically occurs at gas rates of 10,000 to 20,000 SCFB.

[0036] In another embodiment of the process of the present invention the hydrodesulfurization process is carried out in two or more-stages.

[0037] The first stage or stages upstream of a stage operated at conditions in accordance with this invention can be operated at conventional operating conditions wherein the more reactive sulfur compounds are removed. At least one subsequent, downstream stage (or stages) is operated in accordance with conditions that include a hydrogen circulation rate of 5 times the chemical hydrogen consumption rate, preferably 10 times the chemical hydrogen consumption rate and most preferably 20 times the chemical hydrogen consumption rate. The conditions in the subsequent or downstream stage or stages also include a feedstock vaporization value of at least 30 mole %, preferably at least 40 mole %, and most preferably at least 50 mole %. Because not all of the stages are exposed to the hydrogen circulation rates and feedstock vaporization rates of the present invention the multi-stage process minimizes overall capital cost, utility consumption and pressure drop. In accordance with the multi-stage embodiment of the present invention a new recycle loop can be added to feed extra gas to one or more of the stages.

[0038] Other operating conditions used in the hydrodesulfurization process of the present invention include an average reaction zone temperature of from about 400° F. to about 750° F., preferably from about 600° F. to about 750° F., and most preferably from about 650° F. to about 750° F. for best results. Reaction temperatures below these ranges can result in less effective hydrodesulfurization. Excessively high temperatures can cause the process to reach a thermodynamic aromatic reduction limit, hydrocracking, catalyst deactivation, product instability, and increase energy costs.

[0039] The process of the present invention generally operates at reaction zone pressures ranging from about 300 psig to about 2,000 psig, more preferably from about 500 psig to about 1,500 psig, and most preferably from about 600 psig to about 1,200 psig for best results. Excessively high reaction pressures increase energy and equipment costs and provide diminishing marginal benefits.

[0040] The process of the present invention generally operates at a liquid hourly space velocity (LHSV) of from about 0.2 hr.⁻¹ to about 10.0 hr.⁻¹, preferably from about 0.5

hr.⁻¹ to about 4.0 hr.⁻¹, and most preferably from about 1.0 hr.⁻¹ to about 2.0 hr.⁻¹ for best results. Excessively high space velocities will result in reduced overall hydrodesulfurization.

[0041] While not wishing to be bound by theory, it is believed that the deep desulfurization achieved by the process of the present invention is possible because the markedly increased hydrogen circulation rate increases the percentage volatilization. For deep desulfurization one needs to remove the remaining "difficult-to desulfurize" species present in the high boiling range fraction of the feedstock. Because of the high volatilization achieved by the process of the invention the remaining liquid phase has a very high concentration of the "difficult-to-desulfurize species." This means that the partial pressure of these sulfur species is increased inasmuch as the partial pressure is a function of the liquid mole fraction and the vapor pressure of the sulfur species.

[0042] Increasing the gas-to-oil rate is known to be beneficial for increasing hydrogen partial pressure and reducing H₂S partial pressure. These effects are well known and are generally accounted for in a process design. But the effects of gas rate on hydrogen and H₂S partial pressures are not large enough to explain the substantially increased deep desulfurization achieved by the process of the present invention in response to the increased gas and vaporization rates.

[0043] It is believed this strong response is due to the effect of changes in the partial vaporization of the feed. In mixed-phase operation, when the gas-to-oil rate is increased, the feed vaporization increases. This increase in feed vaporization increases the liquid mole fractions, the partial pressures, and the reaction rates of the high-boiling sulfur-containing hydrocarbons that need to be removed to achieve the deep desulfurization of the present invention.

[0044] It is believed this effect becomes very significant as desulfurization severity is increased to produce ultra-low sulfur diesel.

[0045] The effect of gas-to-oil ratio and feed vaporization on desulfurization of an individual sulfur compound can be described by the following equation:

$$k_{\text{mixedphase}} = k_{\text{vaporphase}} \times \frac{P_v / P_t}{1 - a + P_v / P_t \left(a + \frac{H}{M} \right)}$$

[0046] where:

[0047] $k_{\text{mixedphase}}$ = 1st order rate constant observed in mixed-phase operation

[0048] $k_{\text{vaporphase}}$ = 1st order rate constant observed in all-vapor phase operation

[0049] P_v = vapor pressure of the sulfur compound

[0050] a = mole fraction of oil feed that is vaporized

[0051] P_t = total pressure

[0052] H = molar flow rate of gas (excluding vaporized oil)

[0053] M = molar flow rate of oil

[0054] This equation assumes that, in mixed phase operation, the liquid and vapor are in phase equilibrium throughout the reactor. The equation accounts for the fact that in mixed phase operation, changes in partial vaporization change the liquid phase mole fractions and the partial pressures of the sulfur-containing reactants.

[0055] When the gas-to-oil rate is increased at constant temperature and pressure in mixed-phase operation, the feed vaporization (a) increases. For a high boiling sulfur compound having a low vapor pressure (with low P_v), the third term in the denominator is very small. For these compounds, the apparent rate constant in mixed-phase operation changes in roughly direct proportion to $1/(1-a)$. So, for example, if the gas-to-oil ratio were increased such that partial vaporization a increases from 0.2 to 0.6, then this factor would change from $1/0.8$ to $1/0.4$, and the reaction rate of the heaviest sulfur compounds would roughly double.

[0056] A physical interpretation of this is that increased gas rate strips light hydrocarbon from the liquid, concentrating the highest-boiling sulfur compounds in the liquid. The liquid phase mole fractions, the partial pressures, and the reaction rates of the high boiling sulfur compounds consequently increase. This effect is largest for the highest boiling sulfur compounds that are being desulfurized in ultra-deep desulfurization. This effect is cumulative to the beneficial effects of increased gas rate on hydrogen and decreased hydrogen sulfide partial pressures.

[0057] Changes In partial vaporization also affect the partial pressures of aromatic and nitrogen-containing inhibitors. This probably also contributes to the observed effects when carrying out the process of the present invention.

[0058] The performance of conventional diesel desulfurization catalysts can be greatly enhanced by carrying out the hydrodesulfurization process in accordance with this invention. The effect is especially large with high-activity NiMo catalysts at deep desulfurization levels. Under these conditions, doubling the gas-to-oil rate can increase the apparent catalyst activity by 80%. In some cases, it is possible to more than triple the apparent catalyst activity by increasing the gas rate.

[0059] The hydrodesulfurization catalysts used in the process of the present invention can be any conventional commercially available distillate hydrodesulfurization catalysts which comprise a hydrogenation component and a catalyst support.

[0060] While not wishing to limit the scope of the present invention, a hydrodesulfurization catalyst support component generally comprises a weakly acidic refractory inorganic oxide. The refractory inorganic oxide can be, but is not limited to catalytically active alumina, silica, and mixtures of silica and alumina with the preferred refractory inorganic oxide being catalytically active alumina. The catalytically active alumina can be gamma alumina, eta alumina, theta alumina, boehmite, or mixtures thereof with the preferred catalytically active alumina being gamma alumina.

[0061] The hydrogenation component of a typical hydrodesulfurization catalyst comprises a Group VIB metal and a Group VIII metal of the Periodic Table of Elements. The Group VIB metals suitable for use in the present invention include chromium, molybdenum and tungsten. The preferred Group VIB metals are molybdenum and tungsten, and preferably molybdenum. The Group VIII metals suitable for use in the present invention include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. The preferred Group VIII metals are cobalt and nickel, preferably nickel. These metals can be present in the catalyst in their elemental form or as their oxides, sulfides, or mixtures thereof.

[0062] Hydrogenation component metals can be deposited or incorporated upon the support by impregnation employing heat-decomposable salts of the Group VIB and VIII metals or other methods known to those skilled in the art such as ion-exchange, with impregnation methods being preferred. Suitable aqueous impregnation solutions include, but are not limited to cobalt nitrate, ammonium molybdate, nickel nitrate, and ammonium meta-tungstate.

[0063] The present invention is described in further detail in connection with the following example, it being understood that the example is for purposes of illustration and not limitation.

EXAMPLE 1

[0064] The FIG. 1 depicts a curve based on various hydrodesulfurization pilot plant runs carried out with a straight run light gas oil having the composition set forth in TABLE I. This feed had a chemical hydrogen consumption rate of 300 SCFB. Five pilot plant runs were carried in a pilot plant having a fixed bed reaction zone, operated isothermally with once-through hydrogen. Process conditions included 812 psig, 650° F., 2 LHSV. The catalyst was a conventional commercially available NiMo distillate hydrodesulfurization catalyst.

[0065] The data point at 900 SCFB pertains to a run carried out in accordance with prior art process conditions, i.e. a hydrogen circulation to consumption ratio of 900:300 and a vaporization rate of less than 30 mole %. The data points at 3000 and 6000 SCFB pertain to runs carried out in accordance with the invention, i.e., hydrogen circulation to consumption ratios of 10, 10, and 20, respectively, and a vaporization rate of greater than 30 mole %. For these examples, the mole % vaporization is 12% at 900 SCFB, 20% at 1500 SCFB, 37% at 3000 SCFB, and 62% at 6000 SCFB. From an inspection of FIG. 1, one can see that increasing the gas-to-oil rate from 900 to 3000 standard cubic feet per barrel, in accordance with the process of the present invention, brought the product sulfur down from 85 ppm to 10 ppm. This corresponds to more than doubling the apparent catalyst activity. Increasing the gas-to-oil rate further from 3000 to 6000 SCFB brought the product sulfur down to 3 ppm. This corresponds to more than tripling the apparent catalyst activity from that achieved at the prior art conditions.

TABLE I

Feedstock	
Specific gravity	0.857
Sulfur, Wt %	0.788
Nitrogen, ppm	123
Hydrogen, wt %	12.84
Carbon, wt %	85.33
Aromatics, wt %	31.1
Distillation	
D-2887	
Degrees C	
IBP	151.8
10	240.5
20	266.7
30	282.0
40	296.2
50	308.5
60	322.0
70	338.3
80	355.8
90	376.7
FBP	424.3

That which is claimed is:

1. A process for hydrodesulfurizing a sulfur-containing distillate feedstock which process comprises contacting said feedstock with hydrogen in a hydrodesulfurization zone in the presence of a hydrodesulfurization zone catalyst at hydrodesulfurization conditions to produce a desulfurized effluent stream wherein said conditions comprise a hydrogen circulation rate of at least 5 times the molar rate of chemical hydrogen consumption and wherein the percent vaporization of the feedstock in the hydrodesulfurization zone is at least 30 mole percent.
2. The process of claim 1 wherein the percent vaporization of the feedstock is at least 40 mole percent.
3. The process of claim 1 wherein the percent vaporization of the feedstock is at least 50 mole percent.
4. The process of claim 1 wherein the hydrogen circulation rate is at least 10 times the molar rate of chemical hydrogen consumption.
5. The process of claim 4 wherein the percent vaporization of the feedstock is at least 40 mole percent.
6. The process of claim 4 wherein the percent vaporization of the feedstock is at least 50 mole percent.

7. The process of claim 1 wherein the hydrogen circulation rate is at least 20 times the molar rate of chemical hydrogen consumption.
8. The process of claim 7 wherein the percent vaporization of the feedstock is at least 40 mole percent.
9. The process of claim 7 wherein the percent vaporization of the feedstock is at least 50 mole percent.
10. The process of claim 1 wherein the effluent from the hydrodesulfurization zone contains less than about 50 ppmw sulfur.
11. The process of claim 4 wherein the effluent from the hydrodesulfurization zone contains less than about 50 ppmw sulfur.
12. The process of claim 7 wherein the effluent from the hydrodesulfurization zone contains less than about 50 ppmw sulfur.
13. The process of claim 1 wherein the effluent from the hydrodesulfurization zone contains less than about 15 ppmw sulfur.
14. The process of claim 4 wherein the effluent from the hydrodesulfurization zone contains less than about 15 ppmw sulfur.
15. The process of claim 7 wherein the effluent from the hydrodesulfurization zone contains less than about 15 ppmw sulfur.
16. The process of claim 1 wherein the effluent from the hydrodesulfurization zone contains less than about 10 ppmw sulfur.
17. The process of claim 4 wherein the effluent from the hydrodesulfurization zone contains less than about 10 ppmw sulfur.
18. The process of claim 7 wherein the effluent from the hydrodesulfurization zone contains less than about 10 ppmw sulfur.
19. The process of claim 1 wherein the hydrodesulfurization zone comprises a multi-stage process, wherein an upstream stage is operated at conventional hydrodesulfurization conditions and a downstream stage is operated at conditions that include a hydrogen circulation rate of at least 5 times the molar rate of chemical hydrogen consumption and wherein the percent vaporization of the feedstock to the downstream stage is at least 30 mole percent.

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