



US 20030111389A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2003/0111389 A1**
Johnson et al. (43) **Pub. Date: Jun. 19, 2003**

(54) **DESULFURIZATION OF MIDDLE
DISTILLATES**

(52) **U.S. Cl.** **208/208 R**; 208/209; 208/213;
208/246; 208/247; 208/249;
208/299

(76) Inventors: **Marvin M. Johnson**, Bartlesville, OK
(US); **Edward L. Sughrue II**,
Bartlesville, OK (US); **Steven A.**
Owen, Kingood, TX (US); **Peter N.**
Slater, Bartlesville, OK (US); **Byron**
G. Johnson, Bartlesville, OK (US)

(57) **ABSTRACT**

Correspondence Address:

**RICHMOND, HITCHCOOK, FISH &
DOLLAR**
P.O. Box 2443
Bartlesville, OK 74005 (US)

(21) Appl. No.: **10/025,050**

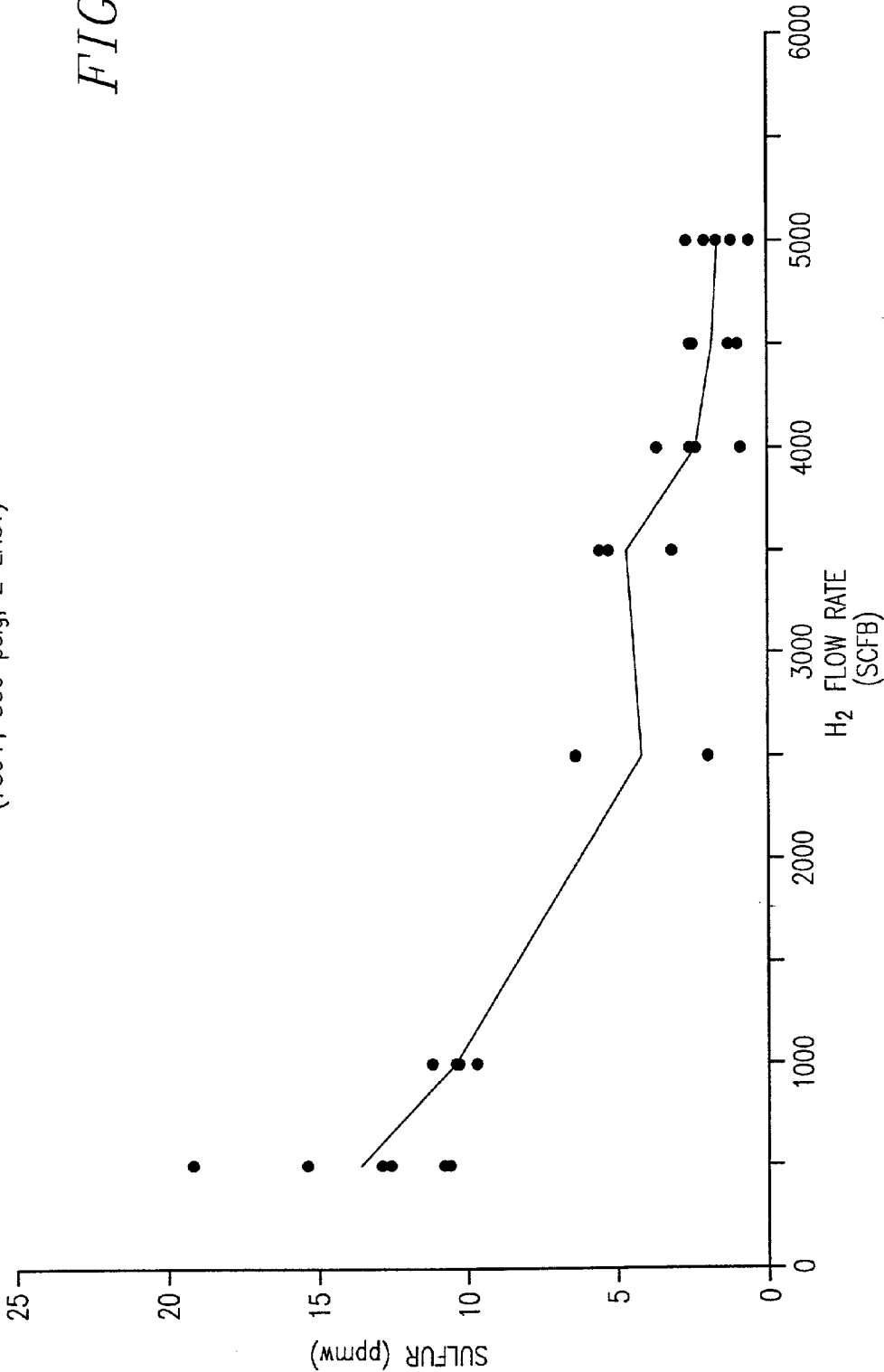
(22) Filed: **Dec. 19, 2001**

Publication Classification

(51) **Int. Cl.⁷** **C10G 45/02**

A process for desulfurizing middle distillates by charging a sulfur-containing middle distillate and a hydrogen-containing diluent to a reaction zone in respective amounts and under reaction conditions sufficient to vaporize substantially all of the sulfur-containing middle distillate present in the reaction zone. In the reaction zone, the vaporized middle distillate is contacted with a sorbent comprising a promoter metal and zinc oxide to thereby provide a desulfurized middle distillate comprising less sulfur than the sulfur-containing middle distillate initially charged to the reaction zone.

DESULFURIZATION OF DIESEL (523ppmw sulfur) at VARIOUS H₂ FLOW RATES
(750°F, 500 psig, 2 LHSV)



DESULFURIZATION OF MIDDLE DISTILLATES

BACKGROUND OF THE INVENTION

[0001] The present invention relates to an improved sorption process for removing sulfur from middle distillates.

[0002] Middle distillates, such as diesel fuel, jet fuel, and kerosene, typically contain a quantity of sulfur. It is well known that high levels of sulfur in such middle distillates can cause pollution when the middle distillates are combusted. High levels of sulfur compounds in automotive fuels, such as diesel fuel, are undesirable because oxides of sulfur present in automotive exhaust may irreversibly poison noble metal catalysts employed in automobile catalytic converters. Emissions from such poisoned catalytic converters may contain high levels of non-combusted hydrocarbons, oxides of nitrogen, and/or carbon monoxide which, when catalyzed by sunlight, form ground level ozone, more commonly referred to as smog. Thus, there exists a need to reduce the sulfur content in middle distillates.

[0003] One problem encountered in conventional processes for desulfurizing middle distillates is the inability to vaporize the middle distillate under suitable desulfurization reaction conditions. Vaporization of the middle distillate during desulfurization is desirable because it allows for more efficient mass transfer of the middle distillate in the desulfurization reaction zone. However, for conventional desulfurization processes, the positive impact of middle distillate vaporization in the reaction zone is outweighed by the negative impact of the reaction conditions (e.g., high temperature and/or high diluent flow rate) required to vaporize the middle distillate.

[0004] Recently, a unique process for removing sulfur from hydrocarbons using a sorbent composition which is both fluidizable and circulatable has been developed (see, U.S. Pat. Nos. 6,254,766 and 6,274,031, the disclosures of which are incorporated herein by reference). In this new type of desulfurization process, it is highly advantageous for substantially all of the hydrocarbon present in the fluidized bed reactor (where the hydrocarbon is contacted with the sorbent) to be vaporized because the presence of liquids in such a fluidized bed reactor causes significant inefficiencies.

[0005] When the hydrocarbon feed to the fluidized bed reactor comprises hydrocarbons having low boiling points, such as catalytically cracked gasoline, the low boiling point hydrocarbon vaporizes easily at the standard operating conditions for the fluidized bed reactor. However, when a higher-boiling point hydrocarbon feed, such as a middle distillate, is charged to the fluidized bed reactor, the middle distillate does not fully vaporize in the reactor under standard reaction conditions. Thus, there exists a need for a middle distillate desulfurization process in which substantially all of the middle distillate in the desulfurization reaction zone is maintained in the vapor phase and the reaction conditions sufficient to achieve such vaporization do not reduce the efficiency of the desulfurization process to an unacceptable level.

SUMMARY OF THE INVENTION

[0006] It is thus an object of the present invention to provide an improved process for desulfurizing middle distillates such as diesel fuel.

[0007] Another object of the present invention is to provide a process for desulfurizing middle distillates in which the desulfurization reaction conditions are sufficient to maintain substantially all of the middle distillates in the desulfurization reaction zone are present in the vapor phase.

[0008] A further object of the present invention is to provide a middle distillate desulfurization process in which the desulfurization reaction conditions are sufficient to maintain substantially all of the middle distillate in the vapor phase, while still providing a high level of sulfur removal.

[0009] It should be noted that the above-listed objects need not all be accomplished by the invention claimed herein and other objects and advantages of the invention will be apparent from the following description of the invention and the appended claims.

[0010] In one aspect of the present invention, a hydrocarbon desulfurization process is provided. The process comprises the steps of: (a) co-feeding a sulfur-containing middle distillate and a hydrogen-containing diluent to a reaction zone in respective amounts and under reaction conditions sufficient to vaporize substantially all of the sulfur-containing middle distillate present in the reaction zone; and (b) contacting the vaporized middle distillate with a sorbent comprising a promoter metal and zinc oxide in the reaction zone to thereby provide a desulfurized middle distillate comprising less than about 50 weight percent of the amount of sulfur in the sulfur-containing middle distillate.

[0011] In accordance with another aspect of the present invention, there is provided a hydrocarbon desulfurization process comprising the steps of: (a) charging a sulfur-containing middle distillate to a reaction zone; (b) simultaneously with step (a), charging a hydrogen-containing diluent to the reaction zone in an amount sufficient to vaporize substantially all of the sulfur-containing middle distillate present in the reaction zone; and (c) contacting the sulfur-containing middle distillate with a sorbent comprising a promoter metal and zinc oxide in the reaction zone under reaction conditions sufficient to convert at least a portion of the zinc oxide to zinc sulfide using sulfur removed from the sulfur-containing middle distillate, thereby providing a desulfurized middle distillate and a sulfurized sorbent.

[0012] In accordance with a further aspect of the present invention, there is provided a desulfurization process comprising the steps of: (a) charging a sulfur-containing middle distillate comprising at least about 50 ppmw sulfur to a reaction zone at a rate in a range of from about 0.5 to about 10 LHSV, said reaction zone maintained at a temperature in a range of from about 650 to about 850° F. and a pressure in a range of from about 250 to about 600 psig; (b) simultaneously with step (a), charging hydrogen to the reaction zone at a rate in a range of from about 2,000 to about 8,000 SCFB to thereby vaporize at least about 95 weight percent of the sulfur-containing middle distillate present in the reaction zone; and (c) contacting the sulfur-containing middle distillate with a sorbent comprising reduced-valence nickel and zinc oxide in the reaction zone to thereby produce a desulfurized middle distillate comprising less than about 50 ppmw sulfur.

[0013] In accordance with a still further aspect of the present invention, there is provided a middle distillate desulfurization process comprising the steps of: (a) charging a sulfur-containing middle distillate to a reaction zone of a

fluidized bed reactor; (b) simultaneously with step (a), charging a hydrogen-containing diluent to the reaction zone at a rate sufficient to cause vaporization of at least about 75 weight percent of the sulfur-containing middle distillate present in the reaction zone; (c) contacting the sulfur-containing middle distillate with a sorbent comprising a promoter metal and zinc oxide in the reaction zone to thereby provide a desulfurized middle distillate comprising less than 50 ppmw sulfur and a sulfurized sorbent comprising zinc sulfide; (d) separating the desulfurized middle distillate and the sulfurized sorbent; (e) contacting at least a portion of the sulfurized sorbent with an oxygen-containing stream in a regeneration zone under regeneration conditions sufficient to convert at least a portion of the zinc sulfide to zinc oxide, thereby providing a regenerated sorbent; (f) contacting at least a portion of the regenerated sorbent with a reducing stream in an activation zone under activation conditions sufficient to reduce the valence of at least a portion of the promoter metal, thereby producing an activated sorbent; and (g) returning at least a portion of the activated sorbent to the reaction zone.

BRIEF DESCRIPTION OF THE DRAWING

[0014] FIG. 1 is a graph showing the effect of varying the hydrogen flow rate in a diesel desulfurization process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] In accordance with one embodiment of the present invention, a novel process is provided for desulfurizing a middle distillate by contacting the vaporized middle distillate with a sorbent comprising a promoter metal and zinc oxide.

[0016] The middle distillate feed employed in the process of the present invention is preferably a mixture of hydrocarbons having a boiling range (ASTM D86-00) of from about 300° F. to about 750° F., more preferably from about 350° F. to about 725° F. The middle distillate feed preferably has a mid-boiling point (ASTM D86-00) of more than about 350° F., more preferably more than about 400° F., and still more preferably more than about 450° F. The middle distillate feed preferably has an API gravity (ASTM D287-92) in a range of from about 20 to about 50, more preferably from about 25 to about 45. The middle distillate feed preferably has a minimum flash point (ASTM D93-99) of at least about 80° F., more preferably at least about 90° F. Examples of suitable middle distillates include, but are not limited to, diesel fuel, jet fuel, kerosene, light cycle oil, and the like, and mixtures thereof.

[0017] Most preferably, the middle distillate feed employed in the desulfurization process of the present invention consists essentially of diesel fuel boiling in a range of from 375° F. to 700° F., having a mid-boiling point of more than 500° F., having an API gravity in a range of from 30 to 38, and having a minimum flash point above 100° F.

[0018] The middle distillate described herein as a suitable feed in the desulfurization process of the present invention may comprise a quantity of aromatics, olefins, and sulfur, as well as paraffins and naphthenes. The amount of aromatics in the middle distillate is preferably in a range of from about 10 to about 90 weight percent aromatics based on the total weight of the middle distillate, more preferably from about

20 to about 80 weight percent aromatics. The amount of olefins in the middle distillate is preferably less than about 10 weight percent olefins based on the total weight of the middle distillate, more preferably less than about 5 weight percent olefins, and most preferably less than 2 weight percent olefins. The amount of atomic sulfur in the middle distillate is generally greater than about 50 parts per million by weight (ppmw) atomic sulfur, more preferably in a range of from about 100 ppmw to about 50,000 ppmw atomic sulfur, and most preferably from 150 ppmw to 2,000 ppmw prior to treatment of the middle distillate fluid with the process of the present invention. It is preferred for at least about 50 weight percent of the atomic sulfur present in the sulfur-containing middle distillate employed in the present invention to be in the form of organosulfur compounds. More preferably, at least about 75 weight percent of the atomic sulfur present in the sulfur-containing middle distillate is in the form of organosulfur compounds, and most preferably at least 90 weight percent of the atomic sulfur is in the form of organosulfur compounds. As used herein, "sulfur" used in conjunction with "ppmw sulfur" or the term "atomic sulfur", denotes the amount of atomic sulfur (about 32 atomic mass units) in the sulfur-containing fluid, not the atomic mass, or weight, of a sulfur compound, such as an organo-sulfur compound.

[0019] As used herein, the term "sulfur" denotes any sulfur compounds normally present in a middle distillate stream, such as diesel fuel. Examples of sulfur compounds which can be removed from a middle distillate stream through the practice of the present invention include, but are not limited to, hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), organic sulfides (R—S—R), organic disulfides (R—S—S—R), thiophenes, substituted thiophenes, organic trisulfides, organic tetrasulfides, benzothiophene, benzothiophenes, alkyl thiophenes, dibenzothiophene, alkyl benzothiophenes, alkyl dibenzothiophenes, and the like, and mixtures thereof as well as heavier molecular weights of the same which are normally present in middle distillates of the types contemplated for use in the desulfurization process of the present invention, wherein each R can be an alkyl, cycloalkyl, or aryl group containing 1 to 10 carbon atoms.

[0020] As used herein, the term "fluid" denotes gas, liquid, vapor and combinations thereof.

[0021] As used herein, the term "vaporized" or "vapor" denotes the state in which the sulfur-containing middle distillate, such as diesel fuel, is primarily in a gas or vapor phase.

[0022] The sorbent composition with which the middle distillate is contacted in order to desulfurize the middle distillate generally comprises a promoter metal and zinc oxide. The sorbent composition employed in the present invention can be prepared in accordance with the sorbent preparation method disclosed in U.S. Pat. Nos. 6,274,533, 6,254,766, and 6,184,176 the disclosures of which are incorporated herein by reference.

[0023] As used herein with reference to the sorbent composition, the term "metal" denotes metal in any form such as elemental metal, metal oxide, or a metal oxide precursor. The promoter metal of the sorbent composition is preferably selected from the group consisting of nickel, cobalt, iron, manganese, tungsten, silver, gold, copper, platinum, zinc,

tin, ruthenium, molybdenum, antimony, vanadium, iridium, chromium, palladium, ruthenium, oxides thereof, precursors to oxides thereof, and combinations thereof. Most preferably, the promoter metal is selected from the group consisting of nickel, nickel oxide, nickel oxide precursors, and combinations thereof. The promoter metal will generally be present in the sorbent composition of the present invention in an amount in a range of from about 1 to about 60 weight percent promoter metal based on the total weight of the sorbent composition, preferably an amount in a range of from about 5 to about 50 weight percent promoter metal, and most preferably in an amount in a range of from 10 to 40 weight percent promoter metal for best sulfur removal.

[0024] Usually, the promoter metal in the common oxidation state of the promoter metal is combined with the zinc oxide portion of the sorbent composition. Alternatively, the promoter metal, or even the entire sorbent composition, can be oxidized after sulfur removal to bring the promoter metal back to the common oxidized state. Prior to use as a sorbent, the number of oxygen atoms associated with the promoter metal must be reduced to form a reduced-valence promoter metal. Consequently, prior to sulfur removal, at least a portion of the promoter metal present in the sorbent composition must be present as a reduced-valence promoter metal. While not wishing to be bound by theory, it is believed that this reduced-valence promoter metal can chemisorb, cleave, or remove sulfur. Thus, either the number of oxygen atoms associated with the promoter metal is reduced or the oxidation state of the promoter metal is a zero-valent metal. For example, if nickel is the promoter metal, nickel oxide (NiO) can be used and the reduced-valence nickel (promoter metal) can be either nickel metal (Ni⁰) or a non-stoichiometric nickel oxide having a formula of NiO_(1-x) wherein 0<x<1. If tungsten is the promoter metal, tungsten oxide (WO₃) can be used and the reduced-valence tungsten (promoter metal) can be either tungsten oxide (WO₂), tungsten metal (W⁰), or a non-stoichiometric tungsten oxide having a formula of WO_(3-y) wherein 0<y<3.

[0025] Of the total quantity of the promoter metal present in the sorbent composition, it is preferred that at least about 10 weight percent of the promoter metal to be present in the form of a reduced-valence promoter metal, i.e., either a zero-valent metal or a non-stoichiometric metal oxide, as described above. More preferably at least about 40 weight percent of the promoter metal is a reduced-valence promoter metal, and most preferably at least 80 weight percent of the promoter metal is a reduced-valence promoter metal for best sorbent activity and sulfur removal. The reduced-valence promoter metal will generally be present in the sorbent composition of the present invention in an amount in a range of from about 0.5 to about 50 weight percent reduced-valence promoter metal based on the total weight of the sorbent composition, preferably in an amount in a range of from about 4 to about 40 weight percent reduced-valence promoter metal, and most preferably in an amount in a range of from 8 to 35 weight percent reduced-valence promoter metal for best sorbent activity and sulfur removal.

[0026] The zinc oxide component of the sorbent composition employed in the desulfurization process of the present invention can be in the form of zinc oxide, such as a dispersion of small crystallites of, or powdered, zinc oxide, or in the form of one or more zinc compounds that are convertible to zinc oxide. Examples of suitable zinc com-

pounds that are convertible to zinc oxide include, but are not limited to, zinc sulfide, zinc sulfate, zinc hydroxide, zinc carbonate, zinc acetate, zinc nitrate, and combinations thereof. Preferably, the zinc oxide is present in the form of small crystallites of zinc oxide for best sorbent activity and sulfur removal. Zinc oxide will generally be present in the sorbent composition of the present invention in an amount in a range of from about 10 to about 90 weight percent zinc oxide based on the total weight of the sorbent composition, preferably in an amount in a range of from about 15 to about 60 weight percent zinc oxide, and most preferably in an amount in a range of from 20 to 55 weight percent zinc oxide for best sorbent activity and sulfur removal.

[0027] When the sorbent composition is exposed to high temperatures (e.g., during calcination), it is preferred for at least a portion of the zinc oxide and the promoter metal to form a substitutional solid solution having the general formula: M_XZn_YO, wherein M is the promoter metal, X is a numerical value in a range of from about 0.5 to about 0.99, and Y is a numerical value in a range of from about 0.01 to about 0.5. Such substitutional solid solution will generally be present in an amount in a range of from about 5 to about 60 percent by weight of the sorbent composition, most preferably from 20 to 40 weight percent. When the sorbent composition comprising the substitutional solid solution is reduced (i.e., activated), it is preferred for at least a portion of the substitutional solid solution to be converted to a reduced metal solid solution having the general formula: M_AZn_B, wherein M is the promoter metal, A is a numerical value in a range of from about 0.7 to about 0.99, and B is a numerical value in a range of from about 0.01 to about 0.3. Such reduced metal solution will generally be present in an amount in a range of from about 5 to about 70 percent by weight of the sorbent composition, most preferably from 25 to 45 weight percent.

[0028] Preferably, the sorbent composition employed in the inventive desulfurization process further comprises a refractory metal oxide such as, for example, silica, alumina, silica-alumina, aluminate, and/or silica-aluminate. The refractory metal oxide such as, for example, silica, alumina, silica-alumina, aluminate, and/or silica-aluminate can enhance the porosity of the resulting composition such that the active sites of the sorbent can be exposed to the reacting mixture.

[0029] Any suitable source of silica may be employed in the sorbent composition such as, for example, diatomite, expanded perlite, silicalite, silicate, silica colloid, flame-hydrolyzed silica, silica gel, precipitated silica, and the like, and combinations thereof. In addition, silicon compounds that are convertible to silica such as silicic acid, ammonium silicate, and the like, and combinations thereof can also be employed. Preferably, the silica source is diatomite or expanded perlite for best sorbent activity and sulfur removal. When the sorbent comprises silica, the silica will generally be present in the sorbent composition in an amount in a range of from about 5 to about 85 weight percent silica based on the total weight of the sorbent composition, preferably in an amount in a range of from about 10 to about 60 weight percent silica, and most preferably in an amount in a range of from 15 to 55 weight percent silica for best sorbent activity and sulfur removal. Generally, perlite comprises silicon dioxide, aluminum oxide, potassium oxide, sodium oxide, calcium oxide, plus trace elements.

[0030] The alumina employed in the preparation of the sorbent composition can be any suitable commercially available alumina material such as, for example, colloidal alumina solutions, hydrated aluminas, peptized aluminas and, generally, those alumina compounds produced by the dehydration of alumina hydrates. The preferred alumina is a hydrated alumina such as, for example, boehmite or pseudo-boehmite for best sorbent activity and sulfur removal. When the sorbent comprises alumina, the alumina will generally be present in the sorbent composition in an amount in a range of from about 1 to about 30 weight percent alumina based on the total weight of the sorbent composition, preferably in an amount in a range of from about 5 to about 20 weight percent alumina, and most preferably in an amount in a range of from 8 to 15 weight percent alumina for best sorbent activity and sulfur removal. When the sorbent composition is exposed to high temperatures (e.g., during calcination) at least a portion, preferably a substantial portion of the alumina is converted to an aluminate, most preferably a zinc aluminate and/or a nickel-zinc aluminate. Preferably, the sorbent composition comprises from about 2 to about 30 weight percent nickel-zinc aluminate, most preferably from 8 to 25 weight percent nickel-zinc aluminate.

[0031] The sorbent composition can additionally comprise a binder. The binder can be any suitable compound that has cement-like, or adhesion, properties which can help to bind the components of the sorbent composition together. Suitable examples of binders include, but are not limited to, cements such as, for example, gypsum plaster, common lime, hydraulic lime, natural cements, portland cements, and high alumina cements, and the like, and combinations thereof. A particularly preferred binder is calcium aluminate. When a binder is present, the amount of binder in the sorbent composition is generally in a range of from about 0.1 to about 50 weight percent binder based on the total weight of the sorbent composition. Preferably, the amount of the binder in the sorbent composition is in a range of from about 1 to about 40 weight percent, and most preferably in a range of from 5 to 30 weight percent for best binding results.

[0032] The sorbent composition employed in the inventive desulfurization process preferably is in the form of a particulate, most preferably a microsphere, having a mean particle size in a range of from about 1 micrometer (micron) to about 500 micrometers, more preferably in a range of from about 10 micrometers to about 300 micrometers for best sulfur removal. As used herein, the term "mean particle size" refers to the size of the particulate material comprising the sorbent as determined by using a RO-TAP Testing Sieve/Shaker, manufactured by W.S. Tyler, Inc. of Mentor, Ohio, or other comparable sieves. To determine mean particle size, the material to be measured is placed in the top of a nest of standard 8 inch diameter stainless steel framed sieves with a pan on the bottom. The material undergoes sifting for a period of about 10 minutes; thereafter, the material retained on each sieve is weighed. The percent retained on each sieve is calculated by dividing the weight of the material retained on a particular sieve by the weight of the original sample. This information is used to compute the mean particle size, by the method outlined in Chapter 3 of *Fluidization Engineering* by Kunii and Levenspiel (1987).

[0033] The middle distillate desulfurization process of the present invention is carried out in the reaction zone of a

reactor under a set of reaction conditions that include total pressure, temperature, liquid hourly space velocity, and diluent flow rate. In the desulfurization process of the present invention, it is preferred that the reaction conditions be sufficient such that the middle distillate, preferably diesel fuel, is maintained in a vapor phase in the reaction zone.

[0034] The reaction conditions at which the reaction zone is maintained preferably include a temperature in a range of from about 650° F. to about 850° F., more preferably from about 700° F. to about 800° F., still more preferably from about 720° F. to about 780° F., and most preferably from 740° F. to 760° F. for best sulfur removal.

[0035] The total pressure at which the reaction zone is maintained is preferably in a range of from about 250 pounds per square inch gauge (psig) to about 600 psig, more preferably from about 350 psig to about 575 psig, still more preferably from about 450 psig to about 550 psig, and most preferably from 475 psig to 525 psig for best sulfur removal.

[0036] As used herein, "liquid hourly space velocity" or "LHSV" is defined as the numerical ratio of the rate at which the middle distillate fluid is charged to the reaction zone in barrels per hour at standard conditions of temperature and pressure (STP) divided by the barrels of sorbent composition contained in the reaction zone to which the middle distillate is charged. In the practice of the present invention, such LHSV should be in a range of from about 0.5 hr⁻¹ to about 10 hr⁻¹, more preferably from about 1.0 hr⁻¹ to about 5 hr⁻¹, still more preferably from about 1.5 hr⁻¹ to about 4.0 hr⁻¹, most preferably from 1.8 hr⁻¹ to 3.0 hr⁻¹ for best sulfur removal.

[0037] An important aspect of the present invention is the employing of a hydrogen-containing diluent as a means for providing improved vaporization of the middle distillate in the reaction zone. The hydrogen-containing diluent employed in the process of the present invention preferably contains at least about 25 volume percent hydrogen based on the total volume of the hydrogen-containing diluent, more preferably at least about 50 volume percent hydrogen, still more preferably at least about 75 volume percent hydrogen, and most preferably more than 95 volume percent hydrogen. The rate at which the hydrogen-containing diluent is charged to the reaction zone is preferably in a range of from about 1,000 standard cubic feet per barrel (SCFB) of the middle distillate fluid to about 10,000 SCFB, more preferably from about 2,000 SCFB to about 8,000 SCFB, still more preferably from about 4,000 SCFB to about 6,000 SCFB, and most preferably from 4,500 SCFB to 5,500 SCFB. It is presently preferred for the middle distillate and hydrogen-containing diluent to be simultaneously introduced into the reaction zone via a common inlet port(s). Most preferably, the middle distillate and hydrogen-containing diluent are combined prior to introduction into the reaction zone, and are thereafter co-fed into the reaction zone.

[0038] Preferably, the reaction conditions employed in the desulfurized process of the present invention are sufficient to provide vaporization of substantially all of the middle distillate present in the reaction zone. Preferably, at least about 75 weight percent of the middle distillate present in the reaction zone is in the vapor phase, more preferably at least about 95 weight percent of the middle distillate is in the vapor phase, and most preferably at least 98 weight percent of the middle distillate is in the vapor phase.

[0039] It is preferred that the desulfurization reaction of the present invention be carried out in the reaction zone of a fluidized bed reactor. As used herein, the term "fluidized bed reactor" denotes a reactor wherein a fluid feed, as defined earlier, can be contacted with solid particles (such as sorbent particles) in a manner such that the solid particles are at least partly suspended within the reaction zone by the flow of the fluid feed through the reaction zone and the solid particles are substantially free to move about within the reaction zone as driven by the flow of the fluid feed through the reaction zone. Although it is preferred for the present invention to be carried out in a fluidized bed reactor, advantages, such as improved mass transfer and reduced pore filling, are also realized when the inventive desulfurization process is carried out in a fixed bed reactor.

[0040] When the sorbent composition is contacted with the vaporized middle distillate in the reaction zone, sulfur compounds, particularly organosulfur compounds, present in the middle distillate are removed from the middle distillate. The sulfur removed from the middle distillate is employed to convert at least a portion of the zinc oxide of the sorbent composition into zinc sulfide. While not wishing to be bound by theory, the inventors postulate that the promoter metal of the sorbent composition functions to facilitate removal of the sulfur from the middle distillate while the zinc oxide functions to facilitate the storage of the sulfur on/in the sorbent composition through the conversion of at least a portion of the zinc oxide to zinc sulfide.

[0041] After sulfur removal in the reaction zone, the fluids in the reaction zone (i.e., the hydrogen-containing diluent and the desulfurized middle distillate) and the solids in the reaction zone (i.e., the sulfurized sorbent composition) can then be separated by any manner or method known in the art for separating a solid from a fluid, preferably a solid from a gas. Examples of suitable separating means for separating solids from gasses include, but are not limited to, cyclonic devices, settling chambers, impingement devices, filters, and combinations thereof.

[0042] In contrast to many conventional sulfur removal processes (e.g., hydrosulfurization), it is preferred that substantially none of the sulfur removed from the middle distillate is converted into hydrogen sulfide. Rather, it is preferred for the fluid effluent (primarily comprising the desulfurized middle distillate and the hydrogen-containing diluent) from the reaction zone to comprise not more than about 200 percent (by weight) of the amount of hydrogen sulfide in the fluid feed (primarily comprising the sulfur-containing middle distillate and the hydrogen-containing diluent) charged to the reactor, more preferably not more than about 150 weight percent of the amount of hydrogen sulfide in the fluid feed, and most preferably less hydrogen sulfide than the fluid feed. It is preferred for the fluid effluent to comprise less than about 50 weight percent of the amount of sulfur in the sulfur-containing middle distillate initially charged to the reaction zone, more preferably less than about 20 weight percent of the amount of sulfur in the fluid feed, and most preferably less than 10 weight percent of the sulfur in the fluid feed. It is preferred for the total sulfur content of the fluid effluent to be less than about 50 parts per million by weight (ppmw) of the total fluid effluent, more preferably less than about 30 ppmw, still more preferably less than about 15 ppmw, and most preferably less than 10 ppmw.

[0043] The desulfurized middle distillate, preferably desulfurized diesel fuel, can thereafter be recovered from the fluid effluent and preferably liquified. Liquification of such desulfurized middle distillate fluid can be accomplished by any method or manner known in the art. The liquified, desulfurized middle distillate preferably comprises at least about 50 weight percent less sulfur than the sulfur-containing middle distillate initially charged to the reaction zone, more preferably at least about 80 weight percent less sulfur, and most preferably at least 90 weight percent less sulfur. The liquified, desulfurized middle distillate preferably comprises less than about 50 ppmw sulfur, more preferably less than about 30 ppmw sulfur, still more preferably less than about 15 ppmw sulfur, and most preferably less than 10 ppmw sulfur.

[0044] After separation of the sulfurized sorbent from the fluid effluent of the reactor, the sulfurized sorbent composition can be regenerated in a regeneration zone by contacting the sulfurized sorbent composition with an oxygen-containing stream under suitable regeneration conditions. The regeneration is preferably carried out at a temperature in a range of from about 100° F. to about 1,500° F., more preferably in a range of from about 800° F. to about 1,200° F. The total pressure in the regeneration zone is preferably in a range of from about 25 pounds per square inch absolute (psia) to about 500 psia. The partial pressure of the oxygen-containing compound is generally in a range of from about 1 percent to about 100 percent of the total pressure. During regeneration, a substantial portion of the promoter metal may be returned to its common oxidized (i.e., unreduced) state. The oxygen-containing stream employed in the regeneration step can be any composition that, when contacted with the sulfurized sorbent composition under the above-described regeneration conditions, promotes the conversion of at least a portion of the zinc sulfide in/on the sulfurized sorbent composition to zinc oxide, as well as burns off any remaining hydrocarbon deposits that might be present on the sulfurized sorbent composition. The oxygen-containing stream employed in the regeneration step can be pure oxygen or any oxygen-containing gas(es) such as air. Regeneration is carried out for a time sufficient to achieve the desired level of sorbent regeneration. Such regeneration can generally be achieved in a time period in a range of from about 0.1 hour to about 24 hours, preferably in a range of from 0.5 hour to 3 hours. These parameters provide for best sorbent regeneration.

[0045] After regeneration, the desulfurized sorbent composition is subjected to reduction (i.e., activating or re-activating) in an activation zone with a reducing agent, preferably hydrogen, so that at least a portion of the unreduced promoter metal of the regenerated sorbent composition is reduced to thereby provide a reduced sorbent composition comprising a reduced-valence promoter metal. Such reduced-valence promoter metal is present in the sorbent composition in an amount that provides for the removal of sulfur from a middle distillate according to the process of the present invention. In general, when practicing the process of the present invention, the reducing (i.e., activating or re-activating) of the desulfurized sorbent composition is carried out at a temperature in a range of from about 100° F. to about 1,500° F. and at a pressure in a range of from about 15 pounds per square inch absolute (psia) to about 1,500 psia. Reduction is carried out for a time sufficient to achieve the desired level of promoter metal reduc-

tion. Such reduction can generally be achieved in a time period in a range of from about 0.01 hour to about 20 hours.

[0046] Following the reducing (i.e., activating or re-activating) of the regenerated, desulfurized sorbent composition, at least a portion of the resulting reduced (i.e., activated) sorbent composition can be returned to the reaction zone.

[0047] In carrying out the process of the present invention, a stripper zone can optionally be inserted before and/or after, preferably before, regenerating the sulfurized sorbent composition in the regeneration zone. A similar stripper zone, preferably utilizing a stripping agent, serves to remove a portion, preferably all, of any hydrocarbon(s) from the sulfurized sorbent composition. Such stripper zone can also serve to remove oxygen and sulfur dioxide from the system prior to introduction of the regenerated sorbent composition into the activation zone. Preferably, the stripping, when employed, is carried out at a total pressure in a range of from about 25 pounds per square inch absolute (psia) to about 500 psia. The temperature for such stripping can be in a range of from about 100° F. to about 1,000° F. Stripping is carried out for a time sufficient to achieve the desired level of stripping. Such stripping can generally be achieved in a time period in a range of from about 0.1 hour to about 4 hours, preferably in a range of from 0.3 hour to 1 hour. The stripping agent is a composition(s) that helps to remove a hydrocarbon(s) from the sulfurized sorbent composition. Preferably, the stripping agent is nitrogen.

[0048] When carrying out the desulfurization process of the present invention, the steps of desulfurizing, regenerating, reducing (i.e., activating or re-activating), and optionally stripping before and/or after such regenerating, can be accomplished in a single zone or vessel or in multiple zones or vessels. The reaction zone can be any zone wherein desulfurizing of a middle distillate fluid, such as diesel fuel, can take place. The regeneration zone can be any zone wherein regenerating or desulfurizing a sulfurized sorbent composition can take place. The activation zone can be any zone wherein reducing (i.e., activating or re-activating), a regenerated, desulfurized sorbent composition can take place. Examples of suitable zones are fixed bed reactors, moving bed reactors, fluidized bed reactors, transport reactors, reactor vessels, and the like.

[0049] When carrying out the process of the present invention in a fixed bed reactor system, the step of desulfurizing, regenerating, reducing and optionally stripping before and/or after such regenerating are accomplished in a single zone or vessel. When carrying out the process of the present invention in a fluidized bed reactor system, the steps of desulfurizing, regenerating, reducing and optionally stripping before and/or after such regenerating can be accomplished in multiple zones or vessels. Preferably, the process of the present invention can be carried out in a fluidized bed reactor system utilizing multiple zones or vessels.

[0050] The following example is presented to further illustrate this invention and is not to be construed as unduly limiting the scope of this invention.

EXAMPLE

[0051] This example demonstrates that the degree of desulfurization of diesel fuel is dramatically increased when a

hydrogen flow rate of more than about 1,000 SCFB is employed to vaporize the diesel in the reaction zone.

[0052] The desulfurization process was carried out by contacting a sorbent composition with diesel in a fixed bed reactor. The sorbent composition comprised about 22 weight percent nickel, about 41 weight percent zinc oxide, about 33 weight percent silica, and about 8 weight percent alumina.

[0053] The diesel feed charged to the reactor comprised a mixture of hydrocarbons which boiled in a range of from about 293° F. to about 742° F. and had a mid-boiling point of about 520° F. The diesel feed had an API gravity (ASTM D287-92) of about 33.2 and contained about 523 parts per million by weight (ppmw) sulfur.

[0054] The fixed bed reactor was a standard steel reactor having a ¾ inch inner diameter and a ¼ inch thermowell.

[0055] The sorbent used in the reactor was in the form of ¼₁₆ inch extrudates. The reactor loading (from bottom up) was the following:

[0056] (1) 5 inches of R268 support alundum;

[0057] (2) 39 grams of 36 grit alundum;

[0058] (3) Dry packed bed of diluted sorbent-30.5 grams of the sorbent mixed with 109 grams of 30/40 grit alundum; and

[0059] (4) 26 grams of 36 grit alundum (pre-heat section).

[0060] The testing procedure consisted of a fixed-bed, downflow feed/hydrogen adsorption, followed by a nitrogen purge, a nitrogen/air regeneration, another nitrogen purge, and a hydrogen reduction. The reaction conditions under which the diesel fuel was contacted with the sorbent composition in the reactor included a temperature of about 750° F., a pressure of about 500 psig, and a diesel flow rate of about 2 LHSV.

[0061] Prior to introduction into the reactor, a hydrogen diluent was combined with the diesel feed. The amount of hydrogen added to the diesel feed prior to introduction into the reactor was varied between about 500 SCFB and about 5,000 SCFB. The degree of diesel desulfurization at the various hydrogen flow rates was determined by analyzing reactor effluent samples for sulfur content using x-ray fluorescence. The results are summarized in Table 1 and FIG. 1.

TABLE 1

Desulfurization of Diesel (523 ppmw sulfur) at Various H ₂ Flow Rates (750° F., 500 psig, 2 LHSV)			
H ₂ Flow Rate (SCFB)	Run #	Sulfur (ppmw)	Average Sulfur in Recovered Liquid Product (ppmw)
500	1	15.4	13.9
	2	12.9	
	3	12.6	
	4	10.6	
	5	19.2	
	6	10.8	
1,000	1	10.4	10.4
	2	10.3	
	3	11.2	
	4	9.7	

TABLE 1-continued

Desulfurization of Diesel (523 ppmw sulfur) at Various H ₂ Flow Rates (750° F., 500 psig, 2 LHSV)			
H ₂ Flow Rate (SCFB)	Run #	Sulfur (ppmw)	Average Sulfur in Recovered Liquid Product (ppmw)
2,500	1	2.0	4.2
	2	6.4	
3,500	1	5.7	4.7
	2	5.4	
	3	3.1	
4,000	1	2.4	2.4
	2	3.7	
	3	0.9	
	4	2.6	
4,500	1	1.3	1.85
	2	2.6	
	3	1.0	
	4	2.5	
5,000	1	2.7	1.66
	2	2.1	
	3	1.2	
	4	1.7	
	5	0.6	

[0062] Table 1 and FIG. 1 show that as the hydrogen flow rate was increased above 1,000 SCFB to vaporize the diesel in the reaction zone, a dramatic increase in sulfur removal was experienced.

[0063] Reasonable variations, modifications, and adaptations can be made within the scope of this disclosure and the appended claims without departing from the scope of this invention.

What is claimed is:

1. A hydrocarbon desulfurization process comprising the steps of:
 - (a) co-feeding a sulfur-containing middle distillate and a hydrogen-containing diluent to a reaction zone in respective amounts and under reaction conditions sufficient to vaporize substantially all of said sulfur-containing middle distillate present in said reaction zone; and
 - (b) contacting the vaporized middle distillate with a sorbent comprising a promoter metal and zinc oxide in said reaction zone to thereby provide a desulfurized middle distillate comprising less than about 50 weight percent of the amount of sulfur in said sulfur-containing middle distillate.
2. A process according to claim 1, wherein said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 1,000 to about 10,000 SCFB.
3. A process according to claim 2, wherein said sulfur-containing middle distillate boils in a range of from about 300 to about 750° F., has a mid-boiling point of more than about 350° F., and comprises more than about 50 ppmw sulfur.
4. A process according to claim 3, wherein said desulfurized middle distillate comprises less than about 50 ppmw sulfur.
5. A process according to claim 4, wherein said reaction conditions in said reaction zone includes a temperature in a range of from about 650 to about 850° F. and a pressure in

a range of from about 250 to about 600 psig, and wherein said sulfur-containing middle distillate enters said reaction zone at a rate in a range of from about 0.5 to about 10 LHSV.

6. A process according to claim 5, wherein said sorbent further comprises an aluminate and said promoter metal is selected from the group consisting of nickel, cobalt, iron, manganese, tungsten, silver, gold, copper, platinum, zinc, tin, ruthenium, molybdenum, antimony, vanadium, iridium, chromium, palladium, oxides thereof, precursors to oxides thereof, and combinations thereof.

7. A process according to claim 1, wherein said hydrogen-containing diluent comprises more than about 25 volume percent hydrogen and said hydrogen-containing diluent enters said reaction zone at a rate of from about 2,000 to about 8,000 SCFB.

8. A process according to claim 7, wherein said sulfur-containing middle distillate boils in a range of from 350 to 725° F., has a mid-boiling point of more than about 400° F., and comprises from about 100 to about 50,000 ppmw sulfur.

9. A process according to claim 8, wherein said desulfurized middle distillate comprises less than about 30 ppmw sulfur.

10. A process according to claim 9, wherein said reaction conditions in said reaction zone include a temperature in a range of from about 700 to about 800° F. and a pressure in a range of from about 450 to about 550 psig, and said sulfur-containing middle distillate enters said reaction zone at a rate of from about 1.0 to about 5 LHSV.

11. A process according to claim 10, wherein said sorbent further comprises zinc aluminate and said promoter metal is a reduced-valence promoter metal having a valence which is at least one valence number lower than the valence of said promoter metal in its common oxidized state.

12. A process according to claim 11, wherein said promoter metal comprises a metal selected from the group consisting of nickel, nickel oxide, nickel oxide precursors, and combinations thereof.

13. A process according to claim 1, wherein said hydrogen-containing diluent comprises at least about 75 volume percent hydrogen, and said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 4,000 to about 6,000 SCFB.

14. A process according to claim 1, wherein at least about 75 weight percent of said sulfur-containing middle distillate present in said reaction zone is present in the vapor phase.

15. A process according to claim 1, wherein said reaction zone is a reaction zone of a fluidized bed reactor.

16. A hydrocarbon desulfurization process comprising the steps of:

- (a) charging a sulfur-containing middle distillate to a reaction zone;
- (b) simultaneously with step (a), charging a hydrogen-containing diluent to said reaction zone in an amount sufficient to vaporize substantially all of said sulfur-containing middle distillate present in said reaction zone; and
- (c) contacting said sulfur-containing middle distillate with a sorbent comprising a promoter metal and zinc oxide in said reaction zone under reaction conditions sufficient to convert at least a portion of said zinc oxide to zinc sulfide using sulfur removed from said sulfur-containing middle distillate, thereby providing a desulfurized middle distillate and a sulfurized sorbent.

17. A process according to claim 16, wherein at least about 95 weight percent of said sulfur-containing middle distillate present in said reaction zone is present in the vapor phase.

18. A process according to claim 17, wherein said promoter metal is selected from the group consisting of nickel, cobalt, iron, manganese, tungsten, silver, gold, copper, platinum, zinc, tin, ruthenium, molybdenum, antimony, vanadium, iridium, chromium, palladium, oxides thereof, precursors to oxides thereof, and combinations thereof.

19. A process according to claim 18, wherein said sorbent further comprises an aluminate.

20. A process according to claim 19, wherein said sulfur-containing middle distillate boils in a range of from about 300 to about 700° F., has a mid-boiling point of more than about 350° F., and comprises more than about 50 ppmw sulfur.

21. A process according to claim 20, wherein said reaction conditions in said reaction zone includes a temperature in a range of from about 650 to about 850° F. and a pressure in a range of from about 250 to about 600 psig, and said sulfur-containing middle distillate enters said reaction zone at a rate in a range of from about 0.5 to about 10 LHSV.

22. A process according to claim 21, wherein said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 1,000 to about 10,000 SCFB.

23. A process according to claim 22, wherein said hydrogen-containing diluent comprises at least about 25 volume percent hydrogen, and said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 2,000 to about 8,000 SCFB.

24. A process according to claim 16, wherein at least 98 weight percent of said sulfur-containing middle distillate present in said reaction zone is present in the vapor phase.

25. A process according to claim 24, wherein said sulfur-containing middle distillate comprises diesel fuel boiling in a range of from about 375 to 700° F., has a mid-boiling point of more than 500° F., has an API gravity in a range of from 30 to 38, has a minimum flash point of at least 100° F., and comprises from about 100 to about 50,000 ppmw sulfur.

26. A process according to claim 25, wherein said reaction conditions in said reaction zone include a temperature in a range of from about 700 to about 800° F. and a pressure in a range of from about 450 to about 550 psig, and said sulfur-containing middle distillate enters said reaction zone at a rate in a range of from about 1.0 to about 5 LHSV.

27. A process according to claim 26, wherein said hydrogen-containing diluent comprises at least 95 volume percent hydrogen.

28. A process according to claim 27, wherein said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 4,000 to about 6,000 SCFB.

29. A hydrocarbon desulfurization process comprising the steps of:

- (a) charging a sulfur-containing middle distillate comprising at least about 50 ppmw sulfur to a reaction zone at a rate in a range of from about 0.5 to about 10 LHSV, said reaction zone maintained at a temperature in a range of from about 650 to about 850° F. and a pressure in a range of about 250 to about 600 psig;
- (b) simultaneously with step (a), charging hydrogen to said reaction zone at a rate in a range of from about 2,000 to about 8,000 SCFB to thereby vaporize at least

about 95 weight percent of said sulfur-containing middle distillate present in said reaction zone; and

- (c) contacting said sulfur-containing middle distillate with a sorbent comprising reduced-valence nickel and zinc oxide in said reaction zone to thereby produce a desulfurized middle distillate comprising less than about 50 ppmw sulfur.

30. A process according to claim 29, wherein said sulfur-containing middle distillate consists essentially of diesel fuel boiling in a range of from 375 to 700° F., having a mid-boiling point of more than 500° F., having a API gravity in a range of from 30 to 38, having a minimum flash point of at least 100° F., and comprising from about 100 to about 50,000 ppmw sulfur.

31. A process according to claim 29, wherein said reaction conditions in said reaction zone includes a temperature in a range of from about 700 to about 800° F. and a pressure in a range of from about 450 to about 550 psig, and said sulfur-containing middle distillate enters said reaction zone at a rate in a range of from about 1.0 to about 5 LHSV.

32. A process according to claim 29, wherein said sorbent further comprises zinc aluminate, and said sorbent comprises said reduced-valence nickel in an amount in a range of from about 0.5 to about 50 weight percent.

33. A process according to claim 32, wherein said reduced-valence nickel is present in said sorbent composition in an amount in a range of from about 4 to about 40 weight percent, and said reduced-valence nickel has a valence of less than 2.

34. A process according to claim 33, wherein said reduced-valence nickel has a valence of zero.

35. A hydrocarbon desulfurization process comprising the steps of:

- (a) charging a sulfur-containing middle distillate to a reaction zone of a fluidized bed reactor;
- (b) simultaneously with step (a), charging a hydrogen-containing diluent to said reaction zone in an amount sufficient to cause vaporization of at least about 75 weight percent of said sulfur-containing middle distillate present in said reaction zone;
- (c) contacting said sulfur-containing middle distillate with a sorbent comprising a promoter metal and zinc oxide in said reaction zone to thereby provide a desulfurized middle distillate comprising less than 50 ppmw sulfur and a sulfurized sorbent comprising zinc sulfide;
- (d) separating said desulfurized middle distillate and said sulfurized sorbent;
- (e) contacting at least a portion of said sulfurized sorbent with an oxygen-containing stream in a regeneration zone under regeneration conditions sufficient to convert at least a portion of said zinc sulfide to zinc oxide, thereby providing a regenerated sorbent;
- (f) contacting at least a portion of said regenerated sorbent with a reducing stream in an activation zone under activation conditions sufficient to reduce the valence of at least a portion of said promoter metal, thereby providing an activated sorbent; and
- (g) returning at least a portion of said activated sorbent to said reaction zone.

36. A process according to claim 35, wherein said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 1,000 to about 10,000 SCFB.

37. A process according to claim 36, wherein said sulfur-containing middle distillate boils in a range of from about 300 to about 750° F. and has a mid-boiling point of more than about 350° F.

38. A process according to claim 37, wherein said reaction conditions in said reaction zone includes a temperature in a range of from about 650 to about 850° F. and a pressure in a range of from about 250 to about 600 psig, and said sulfur-containing middle distillate enters said reaction zone at a rate of from about 0.5 to about 10 LHSV.

39. A process according to claim 38, wherein said promoter metal is selected from the group consisting of nickel, cobalt, iron, manganese, tungsten, silver, gold, copper, platinum, zinc, tin, ruthenium, molybdenum, antimony, vanadium, iridium, chromium, palladium, oxides thereof, precursors to oxides thereof, and combinations thereof.

40. A process according to claim 39, wherein said sorbent further comprises an aluminate.

41. A process according to claim 40, wherein said reaction zone, said regeneration zone, and said activation zone are located in separate vessels.

42. A process according to claim 35, wherein said hydrogen-containing diluent comprises at least 95 volume percent hydrogen, and said hydrogen-containing diluent enters said reaction zone at a rate in a range of from about 4,000 to about 6,000 SCFB.

43. A process according to claim 42, wherein said sulfur-containing middle distillate consists essentially of diesel fuel boiling in a range of from 375 to 700° F., having a mid-boiling point of more than 500° F., having API gravity in a range of from 30 to 38, having a minimum flash point of at least 100° F., and comprising from about 100 to about 50,000 ppmw sulfur.

44. A process according to claim 43, wherein at least 95 weight percent of said sulfur-containing middle distillate present in said reaction zone is present in the vapor phase.

45. A process according to claim 44, wherein said sorbent further comprises zinc aluminate.

46. A process according to claim 45, wherein at least 10 weight percent of said promoter metal is present in the form of a reduced-valence promoter metal, and said reduced-valence promoter metal has a valence which is at least one valence number lower than the valence of said promoter metal in its common oxidized state.

47. A process according to claim 46, wherein said promoter metal is selected from the group consisting of nickel, nickel oxide, nickel oxide precursors, and combinations thereof.

48. A process according to claim 47, wherein said reduced-valence promoter metal has a valence of zero.

* * * * *