

OXIDATIVE DESULFURIZATION PROCESS

5 FIELD OF THE INVENTION

The present invention relates to fuels for transportation which are derived from natural petroleum, particularly processes for the production of components for refinery blending of transportation fuels which are liquid at ambient conditions. More specifically, it relates to a process for making such fuels which includes oxidation of a petroleum distillate
10 in order to oxidize nitrogen and/or sulfur-containing organic impurities therein, by contacting the petroleum distillate with an oxygen-containing gas at oxidation conditions in the presence of a heterogeneous catalyst.

BACKGROUND OF THE INVENTION

15 It is well known that internal combustion engines have revolutionized transportation following their invention during the last decades of the 19th century. While others, including Benz and Gottlieb Wilhelm Daimler, invented and developed engines using electric ignition of fuel such as gasoline, Rudolf C. K. Diesel invented and built the diesel engine which employs compression for auto-ignition of the fuel in order to utilize low-cost organic fuels.
20 Development of improved diesel engines for use in transportation has proceeded hand-in-hand with improvements in diesel fuel compositions. Modern high performance diesel engines demand ever more advanced specification of fuel compositions, but cost remains an important consideration.

At the present time most fuels for transportation are derived from natural petroleum.
25 Indeed, petroleum as yet is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. While compositions of natural petroleum or crude oils are significantly varied, all crudes contain sulfur compounds and most contain nitrogen compounds which may also contain oxygen, but oxygen content of most crude is low. Generally, sulfur concentration in crude is less than about 8 percent, with most crude having
30 sulfur concentrations in the range from about 0.5 to about 1.5 percent. Nitrogen concentration is usually less than 0.2 percent, but it may be as high as 1.6 percent.

Crude oil seldom is used in the form produced at the well, but is converted in oil refineries into a wide range of fuels and petrochemical feedstocks. Typically fuels for transportation are produced by processing and blending of distilled fractions from the crude
35 to meet the particular end use specifications. Because most of the crudes available today in large quantity are high in sulfur, the distilled fractions must be desulfurized to yield products

which meet performance specifications and/or environmental standards. Sulfur-containing organic compounds in fuels continue to be a major source of environmental pollution. During combustion they are converted to sulfur oxides, which in turn, give rise to sulfur oxyacids and, also, contribute to particulate emissions.

5 Even in newer, high performance diesel engines combustion of conventional fuel produces smoke in the exhaust. Oxygenated compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most such compounds have high vapor pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality,
10 as indicated by their cetane numbers. Furthermore, other methods of improving diesel fuels by chemical hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel pumps, injectors and other moving parts which come in contact with the fuel under high pressures.

15 Distilled fractions used for fuel or a blending component of fuel for use in compression ignition internal combustion engines (Diesel engines) are middle distillates that usually contain from about 1 to 3 percent by weight sulfur. In the past a typical specification for Diesel fuel was a maximum of 0.5 percent by weight. By 1993 legislation in Europe and United States limited sulfur in Diesel fuel to 0.3 weight percent. By 1996 in Europe and
20 United States, and 1997 in Japan, maximum sulfur in Diesel fuel was reduced to no more than 0.05 weight percent. This worldwide trend must be expected to continue to even lower levels for sulfur.

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
25 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
30 fuels and in particular diesel fuel within the timeframes prescribed by the regulatory authorities.

In one aspect, pending introduction of new emission regulations in California and other jurisdictions has prompted significant interest in catalytic exhaust treatment. Challenges of applying catalytic emission control for the diesel engine, particularly the
35 heavy-duty diesel engine, are significantly different from the spark ignition internal combustion engine (gasoline engine) due to two factors. First, the conventional three-way

catalyst (TWC) catalyst is ineffective in removing NO_x emissions from diesel engines, and second, the need for particulate control is significantly higher than with the gasoline engine.

Several exhaust treatment technologies are emerging for control of Diesel engine emissions, and in all sectors the level of sulfur in the fuel affects efficiency of the technology.

5 Sulfur is a catalyst poison that reduces catalytic activity. Furthermore, in the context of catalytic control of Diesel emissions, high fuel sulfur also creates a secondary problem of particulate emission, due to catalytic oxidation of sulfur and reaction with water to form a sulfate mist. This mist is collected as a portion of particulate emissions.

Compression ignition engine emissions differ from those of spark ignition engines
10 due to the different method employed to initiate combustion. Compression ignition requires combustion of fuel droplets in a very lean air/fuel mixture. The combustion process leaves tiny particles of carbon behind and leads to significantly higher particulate emissions than are present in gasoline engines. Due to the lean operation the CO and gaseous hydrocarbon emissions are significantly lower than the gasoline engine. However,
15 significant quantities of unburned hydrocarbon are adsorbed on the carbon particulate. These hydrocarbons are referred to as SOF (soluble organic fraction).

While an increase in combustion temperature can reduce particulate emissions, this leads to an increase in NO_x emission by the well-known Zeldovitch mechanism. Thus, it becomes necessary to trade off particulate and NO_x emissions
20 to meet emissions legislation.

Available evidence strongly suggests that ultra-low sulfur fuel is a significant technology enabler for catalytic treatment of diesel exhaust to control emissions. Fuel sulfur levels of below 15 ppm, likely, are required to achieve particulate levels below 0.01 g/bhp-hr. Such levels would be very compatible with catalyst
25 combinations for exhaust treatment now emerging, which have shown capability to achieve NO_x emissions around 0.5 g/bhp-hr. Furthermore, NO_x trap systems are extremely sensitive to fuel sulfur and available evidence suggests that they would need sulfur levels below 10 ppm to remain active.

In the face of ever-tightening sulfur specifications in transportation fuels, sulfur
30 removal from petroleum feedstocks and products will become increasingly important in years to come.

Conventional hydrodesulfurization (HDS) catalysts can be used to remove a major portion of the sulfur from petroleum distillates for the blending of refinery transportation fuels, but they are not efficient for removing sulfur from compounds where the sulfur atom is
35 sterically hindered as in multi-ring aromatic sulfur compounds. This is especially true where

the sulfur heteroatom is doubly hindered (e.g., 4,6-dimethyldibenzothiophene). These hindered dibenzothiophenes predominate at low sulfur levels such as 50 to 100 ppm and would require severe process conditions to be desulfurized. Using conventional hydrodesulfurization catalysts at high temperatures would cause yield loss, faster catalyst coking, and product quality deterioration (e.g., color). Using high pressure requires a large capital outlay.

In order to meet stricter specifications in the future, such hindered sulfur compounds will also have to be removed from distillate feedstocks and products. There is a pressing need for economical removal of sulfur from distillates and other hydrocarbon products.

The art is replete with processes said to remove sulfur from distillate feedstocks and products. One known method involves the oxidation of petroleum fractions containing at least a major amount of material boiling above very high-boiling hydrocarbon materials (petroleum fractions containing at least a major amount of material boiling above about 550° F.) followed by treating the effluent containing the oxidized compounds at elevated temperatures to form hydrogen sulfide (500° F. to 1350° F.) and/or hydroprocessing to reduce the sulfur content of the hydrocarbon material. See, for example, U.S. Patent Number 3,847,798 (Jin Sun Yoo, et al) and U.S. Patent Number 5,288,390 (Vincent A. Durante). Such methods have proven to be of only limited utility since only a rather low degree of desulfurization is achieved. In addition, substantial loss of valuable products may result due to cracking and/or coke formation during the practice of these methods. Therefore, it would be advantageous to develop a process which gives an increased degree of desulfurization while decreasing cracking or coke formation.

U.S. Patent 6,087,544 (Robert J. Wittenbrink et al.) relates to processing a distillate feedstream to produce distillate fuels having a level of sulfur below the distillate feedstream. Such fuels are produced by fractionating a distillate feedstream into a light fraction, which contains only from about 50 to 100 ppm of sulfur, and a heavy fraction. The light fraction is hydrotreated to remove substantially all of the sulfur therein. The desulfurized light fraction, is then blended with one half of the heavy fraction to produce a low sulfur distillate fuel, for example 85 percent by weight of desulfurized light fraction and 15 percent by weight of untreated heavy fraction reduced the level of sulfur from 663 ppm to 310 ppm. However, to obtain this low sulfur level only about 85 percent of the distillate feedstream is recovered as a low sulfur distillate fuel product.

U.S. Patent Application Publication 2002/0035306 A1 (Gore et al.) discloses a multi-step process for desulfurizing liquid petroleum fuels that also removes nitrogen-containing compounds and aromatics. The process steps are thiophene extraction; thiophene

oxidation; thiophene-oxide and dioxide extraction; raffinate solvent recovery and polishing; extract solvent recovery; and recycle solvent purification.

The Gore et al. process seeks to remove 5-65% of the thiophenic material and nitrogen-containing compounds and parts of the aromatics in the feedstream prior to the oxidation step. While the presence of aromatics in diesel fuel tends to suppress cetane, the Gore et al. process requires an end use for the extracted aromatics. Further, the presence of an effective amount of aromatics serves to increase the fuel density (Btu/gal) and enhance the cold flow properties of diesel fuel. Therefore it is not prudent to extract an inordinate amount of the aromatics.

With respect to the oxidation step, the oxidant is prepared in situ or is previously formed. Operating conditions include a molar ratio of H_2O_2 to S between about 1:1 and 2.2:1; acetic acid content between about 5 and 45% of feed, solvent content between 10 and 25% of feed, and a catalyst volume of less than about 5,000 ppm sulfuric acid, preferably less than 1,000 ppm. Gore et al. also discloses the use of an acid catalyst in the oxidation step, preferably sulfuric acid. The use of sulfuric acid as an oxidizing acid is problematic in that corrosion is a concern when water is present and hydrocarbons can be sulfonated when a little water is present.

According to Gore et al. the purpose of the thiophene-oxide and dioxide extraction step is to remove more than 90% of the various substituted benzo- and dibenzo thiophene-oxides and N-oxide compounds plus a fraction of the aromatics with an extracting solvent that is aqueous acetic acid with one or more co-solvents.

U.S. Patent 6,368,495 B1 (Kocal et al.) also discloses a multi-step process for the removal of thiophenes and thiophene derivatives from petroleum fractions. This subject process involves the steps of contacting a hydrocarbon feed stream with an oxidizing agent followed by the contact of the oxidizing step effluent with a solid decomposition catalyst to decompose the oxidized sulfur-containing compounds thereby yielding a heated liquid stream and a volatile sulfur compound. The subject patent discloses the use of oxidizing agents such as alkyl hydroperoxides, peroxides, percarboxylic acids, and oxygen.

WO 02/18518 A1 (Rappas et al) discloses a two-stage desulfurization process which is utilized downstream of a hydrotreater. The process involves an aqueous formic acid based, hydrogen peroxide biphasic oxidation of a distillate to convert thiophenic sulfur to corresponding sulfones. During the oxidation process, some sulfones are extracted into the oxidizing solution. These sulfones are removed from the hydrocarbon phase by a subsequent phase separation step. The hydrocarbon phase containing remaining sulfones is then subjected to a liquid-liquid extraction or solid adsorption step.

The use of formic acid in the oxidation step is not advisable. Formic acid is relatively more expensive than acetic acid. Further, formic acid is considered a "reducing" solvent and can hydride certain metals thereby weakening them. Therefore, exotic alloys are required to handle formic acid. These expensive alloys would have to be used in the solvent recovery section and storage vessels. The use of formic acid also necessitates the use of high temperatures for the separation of the hydrocarbon phase from the aqueous oxidant phase in order to prevent the appearance of a third precipitated solid phase. It is believed this undesirable phase can be formed due to the poor lipophilicity of formic acid. Therefore at lower temperatures, formic acid cannot maintain in solution some of the extracted sulfones.

U.S. Patent 6,171,478 B1 (Cabrera et al.) discloses yet another complex multi-step desulfurization process. Specifically, the process involves a hydrodesulfurization step, an oxidizing step, a decomposition step, and a separation step wherein a portion of the sulfur-oxidated compounds are separated from the effluent stream of the decomposition step. The aqueous oxidizing solution used in the oxidizing step preferably contains acetic acid and hydrogen peroxide. Any residual hydrogen peroxide in the oxidizing step effluent is decomposed by contacting the effluent with a decomposition catalyst.

The separation step is carried out with a selective solvent to extract the sulfur-oxidated compounds. Per the teachings of Cabrera et al. the preferred selective solvents are acetonitrile, dimethyl formamide, and sulfolane.

A number of solvents have been proposed for removing the oxidized sulfur compounds. For example, in U.S. Patent 6,160,193 (Gore) teaches the use of a wide variety of solvents suitable for use in the extraction of sulfones. The preferred solvent is Dimethylsulfoxide (DMSO).

A study of a similar list of solvents used in the extraction of sulfur compounds was published by Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. "Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction" Energy & Fuels 2000, 14, 1232. That list is displayed below:

N,N-Dimethylformamide (DMF)

Methanol

Acetonitrile

Sulfolane

Gore states that there is a relationship between the solvent's polarity with the solvent's extraction efficiency. All of the solvents listed in the patent and the paper are desirably immiscible with the diesel. They are all characterized as either polar protic or aprotic solvents.

WO 01/32809 discloses another process for selectively oxidizing distillate fuel or middle distillates. The subject reference discloses that oxidized distillate fuels such that hydroxyl and or carbonyl groups are chemically bound to paraffinic molecules in the fuel results in a reduction in particulates generated upon combustion of the fuel versus
5 unoxidized fuel. The reference discloses a process for selectively oxidizing saturated aliphatic or cyclic compounds in the fuel in the presence of various titanium containing silicon based zeolites with peroxides, ozone or hydrogen peroxide such that hydroxyl or carbonyl groups are formed.

U.S. Patent 6,402,939 B1 (Yen et al.) discloses a process for the oxidative
10 desulfurization of fossil fuels using ultrasound. Briefly liquid fossil fuel is combined with an acidic aqueous solution comprising water and hydroperoxide to form a multiphase reaction mixture followed by applying ultrasound to the multiphase reaction medium for a time sufficient to cause oxidation of sulfides to sulfones with are subsequently extracted.

U.S. Patent Application Publication 2001/0015339 A1 (Sherman) discloses a method
15 of removing sulfur compounds from diesel fuel that involves forming oxidizing gas into sub micron size bubbles and dispersing these bubbles into flowing diesel fuel to oxidize the sulfur compounds into sulfoxides and/or sulfones.

In view of the above, it is clear that there is a need for a less complex, economic distillate or diesel desulfurization process that does not employ expensive hydrotreating
20 technologies involving greater hydrogen useage or oxidation technologies that employ the use of expensive chemical oxidizing agents and avoids the attendant complex handling and corrosion issues.

The present invention provides for a relatively simple selective desulfurization process wherein a distillate feedstock is contacted with an oxygen-containing gas at
25 oxidation conditions in the presence of a heterogeneous catalyst comprising a titanium-containing composition whereby the sulfur-containing compounds in the distillate feedstock are converted to their corresponding sulfones or sulfoxides a portion of which are then adsorbed on to the titanium-containing composition.

30 SUMMARY OF THE INVENTION

The process of the present invention involves reducing the sulfur content of a distillate feedstock containing sulfur-containing organic impurities to produce a refinery transportation fuel or blending components for refinery transportation fuel, by
35 contacting the feedstock with an oxygen-containing gas in an oxidation/adsorption zone at oxidation conditions in the presence of a heterogeneous oxidation catalyst comprising a titanium-containing composition whereby the sulfur-containing

compounds are converted to sulfones and/or sulfoxides a portion of which are subsequently adsorbed on to the titanium-containing composition. A fuel or blending component having a reduced sulfur content is then recovered from the oxidation zone. The sulfones and/or sulfoxide can be further removed from the catalyst for
5 further processing whereby the catalyst is regenerated for reuse in the process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic flow sheet of an embodiment of the present invention.

10 Figure 2 shows a schematic flow sheet of another embodiment of the present invention.

Figure 3 shows a plot of percentage desulfurization versus hours on stream including the effect of adding an oxygen containing gas to the process in accordance with the invention.

15 Figure 4 shows desulfurization activity of fresh titanium silicate catalyst versus the performance of regenerated titanium silicates as a function of hours on steam.

Figure 5 shows the desulfurization activity of two oxidation catalysts regenerated in accordance with the invention.

20 Figure 6 shows the effect of oxygen content on desulfurization carried out in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Suitable feedstocks generally include refinery streams boiling at a temperature range from about 50°C to about 650°C, preferably 150°C to about 400°C, and more preferably
25 between about 175°C and about 375°C at atmospheric pressure for best results. These streams include, but are not limited to, virgin light middle distillate, virgin heavy middle distillate, fluid catalytic cracking process light catalytic cycle oil, coker still distillate, hydrocracker distillate, jet fuel, vacuum distillates and the collective and individually hydrotreated embodiments of these streams. The preferred streams are the collective and
30 individually hydrotreated embodiments of fluid catalytic cracking process light catalytic cycle oil, coker still distillate, and hydrocracker distillate.

It is also anticipated that one or more of the above distillate streams can be combined for use as feedstock to the process of the invention. In many cases performance of the refinery transportation fuel or blending components for refinery transportation fuel
35 obtained from the various alternative feedstocks may be comparable. In these cases,

logistics such as the volume availability of a stream, location of the nearest connection and short-term economics may be determinative as to what stream is utilized.

In one aspect, this invention provides for the production of refinery transportation fuel or blending components for refinery transportation fuel from a hydrotreated petroleum distillate. Such a hydrotreated distillate is prepared by hydrotreating a petroleum distillate material boiling between about 50°C and about 650°C by a process which includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate; optionally fractionating the hydrotreated petroleum distillate by distillation to provide at least one low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction. In accordance with one embodiment of the process of the present invention the hydrotreated distillate or the low-boiling component can be used as suitable feedstocks for the process of the present invention.

Generally, useful hydrogenation catalysts comprise at least one active metal, selected from the group consisting of the d-transition elements in the Periodic Table, each incorporated onto an inert support in an amount of from about 0.1 percent to about 30 percent by weight of the total catalyst. Suitable active metals include the d-transition elements in the Periodic Table elements having atomic number in from 21 to 30, 39 to 48, and 72 to 78.

The catalytic hydrogenation process may be carried out under relatively mild conditions in a fixed, moving fluidized or ebullient bed of catalyst. Preferably a fixed bed or plurality of fixed beds of catalyst is used under conditions such that relatively long periods elapse before regeneration becomes necessary, for example an average reaction zone temperature of from about 200°C to about 450°C, preferably from about 250°C to about 400°C, and most preferably from about 275°C to about 350°C for best results, and at a pressure within the range of from about 6 to about 160 atmospheres.

A particularly preferred pressure range within which the hydrogenation provides extremely good sulfur removal while minimizing the amount of pressure and hydrogen required for the hydrodesulfurization step are pressures within the range of 20 to 60 atmospheres, more preferably from about 25 to 40 atmospheres.

Hydrogen circulation rates generally range from about 500 SCF/Bbl to about 20,000 SCF/Bbl, preferably from about 2,000 SCF/Bbl to about 15,000 SCF/Bbl, and most preferably from about 3,000 to about 13,000 SCF/Bbl for best results. Reaction pressures and hydrogen circulation rates below these ranges can result in higher catalyst deactivation rates resulting in less effective desulfurization, denitrogenation, and dearomatization.

Excessively high reaction pressures increase energy and equipment costs and provide diminishing marginal benefits.

The hydrogenation process typically operates at a liquid hourly space velocity of from about 0.2 hr⁻¹ to about 10.0 hr⁻¹, preferably from about 0.5 hr⁻¹ to about 3.0 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 hydrogenation.

Further reduction of such heteroaromatic sulfides from a distillate petroleum fraction by hydrotreating would require that the stream be subjected to very severe catalytic hydrogenation in order to convert these compounds into hydrocarbons and hydrogen sulfide (H₂S). Typically, the larger any hydrocarbon moiety is, the more difficult it is to hydrogenate the sulfide. Therefore, the residual organo-sulfur compounds remaining after a hydrotreatment are the larger and most structurally hindered heteroaromatics.

Where the feedstock is a high-boiling distillate fraction derived from hydrogenation of a refinery stream, the refinery stream can be a material boiling between about 200°C and about 425°C. Preferably the refinery stream can be a material boiling between about 250°C and about 400°C, and more preferably boiling between about 275°C and about 375°C.

Useful distillate fractions for hydrogenation can be any one, several, or all refinery streams boiling in a range from about 50°C to about 650°C, preferably 150°C to about 400°C, and more preferably between about 175°C and about 375°C at atmospheric pressure. 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 400°C are generally more profitably processed as fluid catalytic cracker feed and converted to gasoline but are amenable for use in the process of the present invention. The presence of heavy hydrocarbon components in distillate fuels is further constrained by distillate fuel end point specifications.

The distillate fractions for hydrogenation 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 percent by weight. The majority of coker distillate and cycle oil aromatics are present as mono-aromatics 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 ranging as high as 20 percent by weight aromatics. Generally, the aromatics content of a combined hydrogenation facility feedstock will range from about 5 percent by weight to about 80

percent by weight, more typically from about 10 percent by weight to about 70 percent by weight, and most typically from about 20 percent by weight to about 60 percent by weight.

Sulfur concentration in distillate fractions useful in the present invention is generally a function of the high and low sulfur crude mix, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation 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 percent by weight elemental sulfur but generally range from about 0.1 percent by weight to about 0.9 percent by weight elemental sulfur.

Nitrogen content of distillate fractions useful in the present invention is also generally a function of the nitrogen content of the crude oil, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher nitrogen distillate feedstocks are generally coker distillate and the catalytic cycle oils. These distillate feedstock components can have total nitrogen concentrations ranging as high as 2000 ppm, but generally range from about 5 ppm to about 900 ppm.

Typically, sulfur compounds in petroleum fractions are relatively non-polar, heteroaromatic sulfides such as substituted benzothiophenes and dibenzothiophenes. At first blush it might appear that heteroaromatic sulfur compounds could be selectively extracted based on some characteristic attributed only to these heteroaromatics. Even though the sulfur atom in these compounds has two, non-bonding pairs of electrons which would classify them as a Lewis base, this characteristic is still not sufficient for them to be extracted by a Lewis acid. In other words, selective extraction of heteroaromatic sulfur compounds to achieve lower levels of sulfur requires greater difference in polarity between the sulfides and the hydrocarbons.

By means of the heterogeneous catalyzed oxidation according to this invention, it is possible to selectively convert these sulfides directly to into, more polar, Lewis basic, oxygenated sulfur compounds such as sulfoxides and sulfones which are then adsorbed on to the titania-silica. Subsequently a desulfurized feed stock is recovered from the oxidation/adsorption zone. It is believed the process of the present invention also results in the oxidation and adsorption of any nitrogen-containing species which can be simultaneously separated with the sulfur-containing species.

Other compounds which also have non-bonding pairs of electrons include amines. Heteroaromatic amines are also found in the same stream that the above sulfides are found.

Amines are more basic than sulfides. The lone pair of electrons functions as a Bronsted - Lowry base (proton acceptor) as well as a Lewis base (electron-donor). This pair of electrons on the atom makes it vulnerable to oxidation in manners similar to sulfides.

In one aspect, this invention provides a process for the production of refinery transportation fuel or blending components for refinery transportation fuel, which includes: providing a distillate feedstock comprising a mixture of hydrocarbons and sulfur-containing organic impurities; contacting the feedstock with an oxygen-containing gas such as oxygen depleted air in an oxidation zone in the presence of an oxidation catalyst comprising titania-silica which also serves as an adsorbent. Because oxygen depleted air can be used in the present invention, the concentration of oxygen can be less than about 21 vol.%. The oxygen-containing stream preferably should have an oxygen content of at least 0.01 vol. %. An effective concentration is from 0.5 to 10 vol. %. The gases can be supplied from air and inert diluents such as nitrogen if required. As those skilled in the art readily recognize, certain compositions are explosive and the composition of oxygen containing stream should be selected to avoid explosive regions. The oxygen-containing gas can be circulated in amounts ranging from 200 to 20,000 standard cubic feet per barrel.

The pressure in the oxidation/adsorption zone can range from ambient to 3000 psig preferably from about 100 psig to about 400 psig, more preferably from about 100 psig to about 300 psig.

The temperature in the oxidation/adsorption zone can range from about 100°F to about 600° F, preferably from about 200 °F to about 500°F and most preferably from about 300°F to about 400°F.

The oxidation/adsorption process of the present invention operates at a liquid hourly space velocity of from about 0.1 hr⁻¹ to about 100 hr⁻¹, preferably from about 0.2 hr⁻¹ to about 50 hr⁻¹, and most preferably from about 0.5 hr⁻¹ to about 10 hr⁻¹ for best results. Excessively high space velocities will result in reduced overall oxidation and adsorption.

Generally, the oxidation/adsorption process of the present invention begins with a distillate feedstock preheating step. The distillate feedstock is preheated in feed/effluent heat exchangers prior to entering a furnace for final preheating to a targeted reaction zone temperature. The distillate feedstock can be contacted with an oxygen-containing stream prior to, during, and/or after preheating.

Since the oxidation reaction is generally exothermic, interstage cooling, consisting of heat transfer devices between fixed bed reactors or between catalyst beds in the same reactor shell, can be employed. At least a portion of the heat generated from the oxidation process can often be profitably recovered for use in the oxidation process. Where this heat recovery option is not available, cooling may be performed through cooling utilities such as

cooling water or air, or through use of a quench stream injected directly into the reactors. Two-stage processes can provide reduced temperature exotherm per reactor shell and provide better oxidation reactor temperature control.

The oxidation/adsorption zone effluent is generally cooled and the effluent stream is directed to a separator device to remove the oxygen-containing gas which can be recycled back to the process. The oxygen-containing gas purge rate is often controlled to maintain a minimum or maximum oxygen content in the gas passed to the reaction zone. Recycled oxygen-containing gas is generally compressed, supplemented if required, with "make-up" oxygen or oxygen-containing gas (preferably air), and injected into the process for further oxidation.

The process of the present invention can be carried out in any sort of gas-liquid-solid reaction zone known to those skilled in the art. For instance, the reaction zone can consist of one or more fixed bed reactors. A fixed bed reactor can also comprise a plurality of catalyst beds. Additionally the reaction zone can be a fluid bed reactor, slurry, or trickle bed reactor. The simplification implied by the use of a heterogeneous catalyst would facilitate a range of less conventional applications for the process of the present invention. For instance, it is contemplated that the process of the invention can be carried out on skid mounted units at terminals or pipelines garage fore courts and on board fuel cell containing vehicles where sulfur sensitive hydrocarbon reformers and fuel cells are employed.

It is believed the heterogeneous catalyzed oxidation according to the present invention results in the direct oxidation of a portion of the sulfur-containing organic impurities to their corresponding sulfones and/or sulfoxides. These sulfones and/or sulfoxides are then adsorbed on to the catalyst.

For the purposes of this disclosure the term "oxidation catalyst" refers to titanium-containing materials such as:

1. Amorphous Titania-Silica materials. These materials are described in the review article by Gao and Wachs in *Catalysis Today*, 51, 1999, 233-254. Ti concentration from 0.001% to 50% atomic. Any surface area, any pore volume.
2. Titanosilicate zeolite materials. Several type of these materials are known in the literature; TS-1, Ti-beta, Ti-ZSM-12, Ti-MCM-41, Ti-HMS, Ti-ZSM-48, TS-2, Ti-MCM-48, Ti-MSU, Ti-SBA-15, Ti-MMM, Ti-MWW, Ti-TUD-1 and Ti-HSM are some of those. These materials were described in the review article entitled "Active sites and reactive intermediates in titanium silicate molecular sieves" by Ratnasamy and Srinivas in *Advances in Catalysis* 48 (2004) 1-169.
3. Titania-Silica mixed oxides containing up to 50% titania.

4. All of the above catalytic materials that were subjected to silylation treatment, as described in Schoebrechts et al. in WO 02/090468.

Preferred effective titanium-containing materials can be selected from the group consisting of titanium silicate, Ti-MCM and Ti-HMS.

The process of the present invention can achieve desulfurization to a level of below about 10 ppmw and can achieve denitrogenation to a level of below about 10 ppmw.

Generally the oxygen-containing gas is contacted with the feedstock in the presence of the oxidation catalyst in the oxidation/adsorption zone until the oxidation/adsorption zone effluent reaches a predetermined sulfur content or breakthrough which indicates the catalyst has reached the desired capacity or loading of the sulfur species, e.g. sulfones or sulfoxides.

The oxidation/adsorption zone is then taken out of service and regenerated. The oxidation catalysts can then be regenerated by a number of procedures. These methods include high temperature oxidation at conditions including a temperature of about 500 to about 1000 degrees C and a pressure of about 0 to about 100 psia in the presence of an oxygen-containing gas; high temperature pyrolysis at conditions including a temperature of about 500 to about 1000 degrees C and a pressure of about 0 to about 100 psia; high temperature hydrotreatment at conditions including a temperature of about 500 to about 700 degrees C and a pressure of about 25 to about 40 atmospheres in the presence of a hydrogen-containing gas; and solvent regeneration.

An effective solvent is methanol. It is believed other polar solvents such as acetonitrile, dimethyl sulfoxide, sulfolane, acetic acid may be similarly effective in restoring the oxidation catalyst essentially back to its initial activity. The solvent regeneration is generally carried out at conditions including a temperature of about 50 to about 400 degrees F and a pressure of about 0 to about 300 psig pressure, and a contact time with the catalyst such that the liquid hourly space velocity of solvent is maintained until sulfur concentration in the effluent extract stream becomes constant indicating that the regeneration has been essentially completed.

Additionally a pressure swing operation can be carried out to regenerate the catalyst at the following conditions including a temperature of about 100 to about 500 degrees F and a pressure of 0 to about 50 psia pressure. Ideally, one oxidation /adsorption zone will be used to desulfurize the feedstock while another oxidation/adsorption zone is being regenerated after desulfurization service.

In order to better communicate the present invention, another preferred aspect of the invention is depicted schematically in Figure 1. Referring to the schematic flow diagram depicted in Figure 1, a liquid feedstock from Feed Tank 10 is passed through conduit 15

where it is preheated and mixed with a diluted air stream 16 which air stream contains about 7 mole percent oxygen or preferably 3 mole percent oxygen.

The preheated mixture of diluted air and feed is then passed to oxidation/adsorption zone 20. Oxidation/adsorption zone 20 may be operated at 325°F, 200 psig pressure and a liquid hourly space velocity of 0.7 hr⁻¹ or preferably 1.0hr⁻¹. The zone can be a fixed bed downflow reactor where the fixed bed contains titania-silica. In the reactor sulfur-containing organic species in the feedstock are oxidized to their corresponding sulfones and/or sulfoxides. These sulfones and/or sulfoxides are then adsorbed to the titania-silica in the oxidation/adsorption zone. The reaction is exothermic and the oxidation/adsorption zone is operated in a manner such that the rise in temperature across the oxidation/adsorption zone preferably does not exceed 25°F. The oxidation/adsorption zone can be sized to handle a 24 hour cycle operation with a feedstock containing up to 500 ppmw sulfur and a product sulfur specification not to exceed 10 ppmw. After a 24-hour operation cycle, oxidation/adsorption zone 20 would be switched off-line in order to regenerate the oxidation catalyst. The effluent stream 21 from Oxidation/adsorption zone 20 is then passed to Reactor effluent separator 30 where a low sulfur product or blending component is recovered in stream 31. A recycle gas stream 32 is passed to Knockout Drum 50 where additional low sulfur product is recovered in stream 53 and gas recycle stream 52 is dried in Dryer 60 and recompressed (Compressor 70) and recycled to the oxidation/adsorption zone after appropriate additions of make-up oxygen.

Figure 2 depicts oxidation/adsorption zone 40 in regeneration mode. In this case methanol is passed through stream 71 from fresh methanol tank 70 to the Oxidation Reactor Vessel 40 in regeneration 40 in order to desorb the adsorbed sulfones and/or sulfoxides. This regeneration process can remove in excess of 99 % of the adsorbed sulfones and/or sulfoxides and essentially restore the oxidation activity and adsorption capacity of the catalyst. The methanol- and sulfone and/or sulfoxides-containing stream, 41 is then passed to a spent methanol tank before it is passed to column 90 where the methanol is recovered in stream 92 from a waste sulfone and/or sulfoxides methanol stream 91. This waste stream is relatively low in volume and can be sent to a hydrocracker, coker, or a distillate hydrotreater or off-site for further processing. The desorption regeneration can be carried out at the same pressure as the oxidation/adsorption. Preferably the desorption regeneration is carried out at a low pressure equivalent to the pressure in the distillation step. The methanol feed rate can be the same feed rate as the hydrocarbon feedstock is fed to the oxidation/adsorption zone. It is believed at least ten times the catalyst volume in solvent is required to carry out the desorption/regeneration process. Subsequent to the desorption step the oxidation/adsorption zone can be dried out to remove any free remaining methanol. After

the drying step the catalyst in the oxidation/adsorption zone can be calcined at 800° F using a 3% oxygen stream and ultimately put back in service.

For a more complete understanding of the present invention, reference should be now be made to the embodiments illustrated in greater detail in the Examples described below.

EXAMPLE 1

A titanium silicate used in the present invention as the oxidation catalyst and sulfone/sulfoxide adsorbent was prepared as follows: 350 grams of tetraethylorthosilicate were added to 500 grams of water. The tetraethylorthosilicate is immiscible with water and formed two layers with the top layer being the tetraethylorthosilicate: 139 grams of 10% in HCl was added which was soluble in the water layer. The two layers were heated with stirring to about 70°C. The initial reaction with the tetraethylorthosilicate formed a single layer which upon further heating formed a clear violet-gel. The gel was dried at room temperature to produce a solid. The solid was washed with 3 liters of water to reduce the amount of Cl. The catalyst was then dried overnight at 100° C. The solid can optionally be calcined at 500° C for 4 hours. The yield of catalyst was 82 grams.

Three titania-silica catalysts prepared as described above were analyzed and were mostly amorphous), but Catalyst A and Catalyst C contained small concentrations of the anatase polymorph of TiO₂ as shown in Table 1.

Table 1

Catalyst	Wt% anatase	Avg. cryst. Size, Å
A	1.4(1)	85
B	-	-
C	1.7(1)	98

The three catalysts were ground in a mortar and pestle. The X-ray powder patterns were measured on a Rigaku diffractometer using the standard configuration. Catalyst A was blended with a known concentration of quartz internal standard in a Spex 8000 mixer/mill, and the pattern re-measured. Quantitative phase analysis was carried out by the Rietveld method using GSAS.

EXAMPLE 2

Experimental Equipment

Pilot-scale units were used to evaluate the performance of the catalyst with a
5 350 ppm-sulfur-containing diesel feed. The pilot-scale reactor consists of a 10.5 inch
length 0.75 O.D. x 0.438 inch I.D. x 0.065 inch wall 316 Stainless Steel tubing. The
reactor temperatures were maintained by three electrically heated sections of the
reactor wall inside an insulated furnace box. The temperatures of these sections
were controlled by a programmable computer with the use of single point
10 thermocouples on each of the reactor wall sections. In addition, a 0.125 inch O.D.
stainless steel thermowell that runs through the middle of the reactor from the top
housed a multi-point thermocouple (three multi-point thermocouple with 2" spacing)
to monitor internal reaction temperature.

The pilot plant reactor consisted of a preheat zone filled with alumina chips,
15 sieved to a Tyler screen mesh size of -20 +40 (USA Standard Testing Sieve by W.S.
Tyler). The second and third heated zones were loaded with 10 cc catalyst crushed
to a Tyler screen mesh size of -20 +40 (USA Standard Testing Sieve by W.S. Tyler).
The remainder of the reactor (temperature zone 4) was filled with alumina chips,
sieved to a Tyler screen mesh size of -20 +40 (USA Standard Testing Sieve by W.S.
20 Tyler) and used as a cool-down zone and to support the catalyst. The reactor was
predominately operated in the down-flow mode, but was also been operated in an
up-flow configuration.

A Brooks flow controller was used to deliver 250 ml min^{-1} 7% oxygen diluted in
nitrogen feed gas to the reactor. An oxygen analyzer installed downstream of the
25 reactor measured the oxygen content of the off-gas at ambient pressure.

A precision syringe-metering pump (ISCO) delivered liquid feed to the reactor. The
feed was preheated to the reaction temperature in the reactor preheat zone, and the
temperature was measured along the centerline by thermocouples in various positions. The
liquid product from the reactor flowed into a cooled high-pressure separator/receiver where
30 7% oxygen in nitrogen was used to maintain the outlet pressure of the reactor at operating
pressure. Reactor pressure was maintained at 200 psig by a GO back pressure regulator on
the off-gas from the separator/receiver. Liquid samples were drained from the high-pressure
receiver/separator and analyzed for sulfur content by a Spectro XEPOS XRF analyzer, Model

XEP01. Nitrogen was determined by chemiluminescence. Sulfur specification was determined with a capillary GC, with a sulfur specific detector

For these experiments, 10 cc of catalyst were charged to the reactor. Feed flow rates were operated to achieve a liquid hydraulic space velocity (standard volume of feed in cc/hour divided by charged volume of catalyst in cc) to range between 1.0 and 2.0 hr⁻¹. The reaction zone temperature was maintained at 320°F +/- 5°F.

Experimental Procedure

After the reactor was charged with catalyst, it was pressurized with 7% oxygen diluted in nitrogen gas at 200 psig and gas flow was established at 250 ml min⁻¹. The catalyst bed was saturated with approximately 50 ml feed. A feed rate of 10-50 ml hour⁻¹ was then initiated. With the gas and liquid feed established, the reactor was slowly heated to the operating temperature of 300-400°F. After the desired operating temperature was achieved, the test begins and liquid product is collected at hourly intervals. The liquid product was then analyzed for sulfur content by a Spectro XEPOS model XEP01 XRF analyzer. The reaction was continued until deactivation of the catalyst or breakthrough occurred.

Procedure for spent catalyst evaluation:

One to two microliters of the methanol extract of spent catalyst were injected via a split injection port at 300°C onto a 30 meter by 0.32mm i.d. fused silica column with a 0.1 micron film of polydimethylsilicone (DB1). Column temperature was held at 40°C for 2 minutes then programmed to increase to 300°C at 10°C/minute intervals. The transfer line from the end of the column to the mass spectrometer ion source was held at 300°C. Mass spectra were obtained at a scan rate of 0.7 seconds per mass decade at either 3000 mass resolving power or 1000 mass resolving power.

Results and Discussion:

Experiments were conducted with a titanium-silicate catalyst using diesel fuel as the feed having the properties set forth in Table 2 below. While the diesel feed was flowing through the catalyst bed, in the beginning of the experiment, only pure nitrogen gas was fed into the reactor. Results in Table 4 below indicate that with no oxygen present in the system, sulfur concentration in the reactor effluent was reduced by 12.92 percent. After several hours on stream, the gas flow was switched to a gas flow made up of 7% volume oxygen in nitrogen. As can be clearly seen from the results, the gaseous molecular oxygen was efficiently utilized by the catalyst to

reduce the sulfur content in the reactor effluent by 74.72 percent. These experimental results clearly demonstrate that the titanium-silicate catalyst was effective in removing sulfur from the feed stream when gaseous oxygen was present in the feed gas. Figure 3 graphically depicts the results of the experimental run.

Additionally, Table 3 below indicates the same sulfur compounds were present in the product as were present in the feed but at a lower concentration. However, GC-MS analysis of methanol extracted hydrocarbons from the spent catalyst revealed the presence of sulfoxides and sulfones in addition to unreacted C1-C4 dibenzothiophenes. Because acid washing would be expected to selectively remove sulfones and sulfoxides from product and essentially none were removed, one can conclude that there were no sulfoxides or sulfones in the product and that they had been adsorbed on to the catalyst.

Table 2

Distillate Feed Composition
Analytical Tests

Feed Inspection

XRF Sulfur, ppm-w	356
Chemiluminescence (ASTM 4629) Nitrogen, ppm-w	233

Sulfur Speciation

1- C1 Benzothiophenes, ppm S	0.30
2- C2 Benzothiophenes, ppm S	2.36
3- C3 Benzothiophenes, ppm S	9.56
4- C4 Benzothiophenes, ppm S	25.42
5- Dibenzothiophene, ppm S	9.31
6- C1 Dibenzothiophenes, ppm S	79.78
7- C2 Dibenzothiophenes, ppm S	115.01
8- C3 Dibenzothiophenes, ppm S	60.47
9- C4 Dibenzothiophenes, ppm S	65.73
total S ppm	367.94

Table 3

	<u>Feed</u>	<u>Product</u>	<u>Acid washed Product</u>
Total sulfur, ppm-w	356	90	70
Sulfur Speciation			
1- C1 Benzothiophenes, ppm S	0.30	0.00	0.00
2- C2 Benzothiophenes, ppm S	2.36	0.02	0.11
3- C3 Benzothiophenes, ppm S	9.56	1.25	1.23
4- C4 Benzothiophenes, ppm S	25.42	5.90	5.43
5- Dibenzothiophene, ppm S	9.31	0.00	0.00
6- C1 Dibenzothiophenes, ppm S	79.78	17.80	16.14
7- C2 Dibenzothiophenes, ppm S	115.01	25.05	22.67
8- C3 Dibenzothiophenes, ppm S	60.47	16.28	14.98
9- C4 Dibenzothiophenes, ppm S	65.73	19.54	16.72
total S ppm	367.94	85.84	77.28

Table 4

Catalyst type	press. psig	temp, °F	LHSV	feed gas	gas flow rate, scfm	product S, ppm	product N, ppm	product O, wt%	product TAN	acid washed product S, ppm	Feed S, ppm	Feed N, ppm	hrs on stream	% desulf	% denitrog
Ti silicate	200	322	1	N ₂	250	310	128				356	233	6.63	12.92%	45.06%
Ti silicate	200	322	1	N ₂	250	310	174	<0.10			356	233	22.00	12.92%	25.32%
Ti silicate	200	323	1	7% O ₂	250	180	176	<0.10			356	233	22.92	49.44%	24.46%
Ti silicate	200	323	1	7% O ₂	250	90	137	<0.10			356	233	23.67	74.72%	41.20%
Ti silicate	200	322	1	7% O ₂	250	120	134	<0.10			356	233	24.34	66.29%	42.49%
Ti silicate	200	322	1	7% O ₂	250	130	138	<0.10			356	233	25.09	63.48%	40.77%
Ti silicate	200	323	1	7% O ₂	250	170	143	0.10			356	233	25.84	52.25%	38.63%
Ti silicate	200	322	1	7% O ₂	250	200	148	0.10			356	233	26.59	43.82%	36.48%
Ti silicate	200	322	1	7% O ₂	250	230	156	0.10			356	233	27.34	35.39%	33.05%
Ti silicate	200	322	1	7% O ₂	250	250	164	0.10			356	233	28.09	29.78%	29.61%
5 none	200	305	1	7% O ₂	250	346	246	0.10	0.03	253	356	233	17.00	2.81%	-5.58%
5 none	200	329	1	7% O ₂	250	345	243	0.10	0.03	266	356	233	43.00	3.09%	-4.29%

EXAMPLE 3

Two different methods were tried for regenerating the deactivated Ti-silicate catalyst. The first regeneration ("A") included heat treating the spent catalyst in flowing nitrogen (572°F) followed by air (950°F) for at least several hours; see Table 5 below. The second regeneration ("B") method involved soaking the catalyst in methanol in a sealed reactor at 310°F for at least several hours followed by calcinations in flowing 7% oxygen in nitrogen at 800°F for at least several hours. These regenerated catalysts were then used to carry out the process of the invention. Results are graphically depicted in Figure 4 and set forth in Table 6 below.

Table 5

Regeneration procedure	Heated in N2 ramping T to 300C. Collected condensate and weighed catalyst. Catalyst further calcined in air to 950F for 4 hr.				
Spent cat before regeneration					
Sulfur, wt% by ICP	0.154				
Carbon, wt%	22.12				
Hydrogen, wt%	3.06				
Nitrogen, wt%	0.22				
Spent cat after regeneration					
Sulfur, wt% by ICP	0.0066				
Carbon, wt%	1.07				
Hydrogen, wt%	0.59				
Nitrogen, ppm-w	72				
Spent catalyst before regen, g	34.56				
Condensate collected during regen, wt	4.68				
Condensate sulfur, ppm-wt					
Condensate oxygen, wt%					

Table 6

5

Fresh				Regeneration A				Regeneration B			
				regenerate with nitrogen at 572F followed by calcination at 950F in air				regenerate with methanol at 310F followed by calcination at 800F in 7% oxygen			
product S, ppm	Feed S, ppm	hrs on stream	% desulf	product S, ppm	Feed S, ppm	hrs on stream	% desulf	product S, ppm	Feed S, ppm	hrs on stream	% desulf
				30	356	0.75	91.57%				
				60	356	1.50	83.15%	35	356	1.00	90.17%
				70	356	2.33	80.34%	62	356	2.00	82.58%
70	356	3.00	80.34%	100	356	3.33	71.91%	70	356	3.00	80.34%
87	356	4.00	75.56%	130	356	4.08	63.48%	108	356	4.00	69.66%
106	356	5.00	70.22%	160	356	4.83	55.06%	138	356	5.00	61.24%
136	356	6.00	61.80%	210	356	5.58	41.01%	173	356	6.00	51.40%
				220	356	6.33	38.20%				

Results indicate that it is possible to regenerate the catalyst after it is deactivated in the oxidation/adsorption zone. At this time, it is believed that the strongly adsorbed oxidized sulfur compounds on the surface of the catalyst are responsible for the catalyst deactivation. It is believed nitrogen compounds that are present in the feed oil and the oxidized nitrogen compounds (in the catalyst assisted oxidation reaction) may also play a role in the catalyst deactivation.

EXAMPLE 3

In this example three separate deactivation runs were carried out.

Table 7 shows that essentially all of the sulfur was either deposited on the catalyst or recovered in the liquid product.

Table 7

Run Description	Three separate deactivation runs at 1.5 hr, 3 hr, and 4.5 hr to mass balance sulfur and determine S,N levels on catalyst.					
	1.5 hr test		3.0 hr test		4.5 hr test	
Catalyst						
Catalyst Description	Ti silicate		Ti silicate		Ti silicate	
Age of Catalyst, hrs	lineout	1.50	lineout	3.00	lineout	4.50
Operating Conditions						
Reaction Temperature, °F	325		325		325	
Pressure, psig	200		200		200	
Gas Feed	7% O ₂ /N ₂		7% O ₂ /N ₂		7% O ₂ /N ₂	
Gas Flow Rate, sccm	250		250		250	
Feed Description	finished diesel		finished diesel		finished diesel	
Feed LHSV	1.0		1.0		1.0	
Analytical Results						
Feed sulfur, ppm-w	335	335	335	335	335	335
Feed total nitrogen, ppm-w	73	73	73	73	73	73
Product nitrogen, ppm-w	55	22	50	16	58	20
Product sulfur, ppm-w	286	60	276	70	284	90
Product weight, g	84.43	17.19	84.02	32.73	83.77	50.96
Absolute sulfur in product, g	0.0241	0.0010	0.0232	0.0023	0.0238	0.0046
Spent Catalyst						
Sulfur, ppm-w	580		1230		1130	
Carbon, wt%	21.83		16.47		24.27	
Hydrogen, wt%	3.08		2.36		3.33	
Nitrogen, wt%	<0.10		<0.10		<0.10	
Carbon, Hydrogen, and nitrogen, combined %	24.91		18.83		27.60	
Calculations						
wet catalyst wt, calculated, g	12.41		11.36		12.80	
Total sulfur on wet catalyst, g	0.0072		0.0140		0.0145	
Total feed processed, g	101.62		116.75		134.73	
Total sulfur processed, g	0.03404		0.03911		0.04513	
Total sulfur in all product cuts, g	0.0252		0.0255		0.0284	
Sulfur mass balance, %	95.11%		#####		94.93%	
hrs on stream	1.5		3.0		4.5	
% desulfurization	82.09%		79.10%		73.13%	
% denitrogenation	69.86%		78.08%		72.60%	

EXAMPLE 4

- 10 Additional runs were carried out using amorphous titanium silicate and a mixture of Ti/MCM and Ti/HMS molecular sieves. Table 8 below and Figure 5 show the results of these runs.

Table 8

hrs on stream	Catalyst type	press. psig	temp, °F	LHSV	feed gas	gas flow rate, sccm	product S, ppm	product N, ppm	Feed S, ppm	Feed N, ppm	% desulf
2.00	Ti/MCM & Ti/HMS soigel	200	318	1	3% O ₂	250	92	203	356	233	74.16%
4.00	Ti/MCM & Ti/HMS soigel	200	318	1	3% O ₂	250	166	160	356	233	53.37%
6.00	Ti/MCM & Ti/HMS soigel	200	318	1	3% O ₂	250	177	163	356	233	50.28%
2.25	Ti silicate	200	321	1	3% O ₂	250	74	44	356	233	79.21%
3.75	Ti silicate	200	321	1	3% O ₂	250	50	28	356	233	85.96%
6.00	Ti silicate	200	321	1	3% O ₂	250	106	47	356	233	70.22%

5

EXAMPLE 5

Figure 6 shows the results of various runs carried out in accordance with the invention wherein oxygen levels were varied and temperatures were varied.

That which is claimed is:

5 1. Process for desulfurizing a distillate feedstock to produce refinery transportation fuel or blending components for refinery transportation fuel wherein the feedstock contains sulfur-containing organic impurities which process comprises:

10 (a) contacting the feedstock with an oxygen-containing gas in an oxidation/adsorption zone at oxidation conditions in the presence of an oxidation catalyst comprising a titanium-containing composition to convert at least a portion of the sulfur-containing organic impurities to sulfones and/or sulfoxides;

 (b) adsorbing the sulfones and/or sulfoxides on to the oxidation catalyst; and

15 (c) recovering an oxidation/adsorption zone effluent having a reduced amount of sulfur-containing impurities.

20 2. The process of claim 1 wherein the oxidation catalyst is regenerated to produce an oxidation catalyst that contains less adsorbed sulfones and/or sulfoxides.

 3. The process of claim 2 wherein the regeneration is carried out by contacting the catalyst with methanol under conditions to desorb the adsorbed sulfones and/or sulfoxides.

25 4. The process of Claim 1 wherein the titanium-containing composition is selected from the group consisting of titanium silicate, Ti-MCM, and Ti-HMS.