

NOVEL PROCESS FOR REMOVING SULFUR FROM FUELS

[0001] This invention relates to a novel process for removing sulfur-containing organic compounds from fuels by oxidative desulfurisation.

5 **[0002]** For many years, growing concerns over environmental pollution caused by the presence of sulfur-containing compounds in hydrocarbon-based fuels such as diesel, gasoline, and kerosene has provided impetus for the development of desulfurisation technology. A high level of sulfur in fuels is undesirable due to the formation of SO_x from the combustion of sulfur-
10 containing compounds. SO_x in turn causes acid rain to form, leading to widespread damage to buildings and disturbing delicate balances in the ecosystem. Furthermore, sulfur compounds in fuels poison the noble metal catalysts used in automobile catalytic converters, causing fuel to be incompletely combusted and thus result in the emission of incompletely
15 combusted hydrocarbons, carbon monoxide, nitrogen oxides in the vehicle exhaust, all of which are precursors of industrial smog.

[0003] To protect the environment against pollution caused by sulfur, governmental agencies have set up guidelines for petroleum refining companies to limit the level of sulfur in commercial fuels. For example, the
20 United States Environmental Protection Agency (EPA) has recently announced plans to reduce sulfur content of diesel fuels from the current 500 parts per million (ppm) to 50 ppm in 2006.

[0004] The industrial removal of sulfur from fuels is generally carried out via the well-established hydro-desulfurization (HDS) process, described for
25 example in the GB Patent 438,354. HDS involves the catalytic treatment of fuel with hydrogen to convert sulfur-containing compounds to hydrogen sulfide, H_2S . H_2S is in turn converted to elemental sulfur by the Claus process. For low point and middle boiling point distillates, the typical HDS reaction requires relatively severe conditions of about 300°C to 400°C and 0.7 to 5
30 MPa.

[0005] It has been found that HDS is less effective in removing certain residual sulfur-containing compounds present in petroleum distillates, particularly heterocyclic sulfur-containing compounds such as thiophenes, benzothiophenes (BT), dibenzothiophenes (DBT), especially DBTs having
5 alkyl substituents on their 4 and/or 6 positions (Ind. Eng. Chem. Res. 2002, 41, 4362-4375), as well as higher homologs of these compounds. One possible reason is that the sulfur atom is sterically hindered by the bulky benzyl groups, thereby making the sulfur atom less accessible to oxidative attack.

10 [0006] Although these heterocyclic sulfur compounds may be removed by optionally increasing the severity of HDS reaction conditions, the onset of other side reactions leading to the formation of coke, degradation of the octane level of the fuel, as well as the accompanying increase in energy and hydrogen consumption, makes the HDS option undesirable from an economic
15 perspective.

[0007] Therefore, alternative processes have been developed to further lower sulfur content of fuels through the removal of residual sulfur-containing compounds from processed fuels, while maintaining or improving fuel performance. The term "deep desulfurisation" is typically applied to such
20 processes.

[0008] In general, deep desulfurisation is carried out on fuels which have already undergone HDS and thus have sulfur contents that have been lowered from the initial level of several thousand ppm to several hundred ppm. Deep desulfurisation is thus distinguished from conventional HDS in that it the
25 oxidation of sulfur occurs at a sulfur concentration that is by comparison much lower. From the perspective of reaction kinetics, reactions that are first order or higher with respect to the reactant become more difficult to carry out as the concentration of the reactant becomes gradually lower.

[0009] One current approach to the deep desulfurisation of fuels include
30 the use of transition metal adsorbents for removing the sulfur compounds, as disclosed in US Patent Application No. 2004/0007506, for example.

[0010] Another approach that has been investigated is oxidative desulfurisation (ODS), in which fuel is contacted with oxidants such as hydrogen peroxide, ozone, nitrogen dioxide, and tert-butyl-hydroperoxide, in order to selectively oxidise the sulfur compounds present in the fuel to polar organic compounds. These polar compounds can be easily separated from the hydrophobic hydrocarbon based fuel via solvent (liquid) extraction using solvents such as alcohols, amines, ketones or aldehydes, for example.

[0011] US Patent 3,847,800 discloses an ODS process in which nitrogen dioxide gas is used as an oxidant to oxidise sulfur-containing compounds in diesel fuel. Methanol and ethanol are subsequently used as non-miscible solvents for extracting the oxidised compounds.

[0012] The European Patent Application No. EP 0 565 324 A1 discloses a method of recovering organic sulfur compounds from liquid oil. The method involves a pure redox-based process between the sulfur compounds and the oxidant. The liquid oil to be processed is treated with an oxidising agent, such as ozone gas, chlorine gas, peracetic acid or hydrogen peroxide to oxidise the sulfur compounds in the oil into sulfones or sulfoxides. Subsequently, the oxidised products are separated using a combination of means such as distillation, solvent extraction and adsorption.

[0013] The use of gaseous or liquid oxidants such as hydrogen peroxide, ozone, dioxirane and ethylene oxide to convert the sulfur compounds present in fuels into sulfones is also disclosed in US Patent 6,160,193. The oxidants are contacted with fuel in liquid phase, and the oxidised products thus formed are subsequently extracted from the fuel by adding dimethyl sulfoxide to the reaction mixture. According to this patent, when hydrogen peroxide is used as oxidant, metal catalysts can be used to accelerate the decomposition of the hydrogen peroxide to form the reactive oxidising species. The dimethyl sulfoxide forms an aqueous phase which is separable from the hydrocarbon phase by gravity separation or centrifugation. Oxidation is reportedly carried out at about 30°C to 100°C at pressures of

about 150 psig (about 12.5 bars) or preferably at a pressure of 30 psig (about 2.5 bars).

[0014] US Patent 6,402,940 further discloses a method for the oxidative removal of sulfur using an oxidising aqueous solution that comprises hydrogen peroxide and formic acid in specific molar ratios. This oxidising solution is mixed with liquid fuel at temperatures of 50 to 130°C, thereby oxidising the sulfur compounds into polar compounds. The polar compounds are subsequently removed by simple extraction and phase separation.

[0015] Finally, the PCT application WO 03/051798 discloses a method for carrying out ODS in which the fuel and oxidant are contacted in the gas-phase. The fuel is first vapourised and then contacted with a supported metal oxide catalyst in the presence of oxygen. Sulfur is liberated from hydrocarbon molecules in the fuel as sulfur dioxide gas, which is subsequently removed with an ion exchange column.

[0016] Nevertheless, despite the developments that have taken place, alternative technologies need to be developed in order to reduce sulfur content in fuels while preferably maintaining/improving fuel performance without significant capital and operating costs. Accordingly, it is an object of the present invention to provide a corresponding process for removing sulfur-containing compounds in fuels in order to obtain fuels that have low sulfur content. It is a further object of the invention to provide a process for the effective removal of sulfur compounds from fuels which are not easily removed through conventional HDS processes, but is still economical to carry out on an industrial scale.

[0017] This object is solved by a process for removing sulfur-containing compounds from fuel, comprising:

contacting the fuel in liquid phase with air to oxidise the sulfur-containing compounds, said contacting being carried out in the presence of at least one transition metal oxide catalyst.

[0018] In oxidative desulfurisation processes, the removal of sulfur-containing compounds from petroleum-based hydrocarbon fuels is carried out

by oxidising the sulfur-containing compounds using a suitable oxidant. The sulfur containing compounds are converted into compounds having increased polarity relative to the fuel, and then subsequently extracted. In the present invention, oxidation is accomplished by contacting liquid fuel with air in the presence of transition metal oxide catalysts that selectively facilitates the oxidation of the residual sulphur compounds.

[0019] One advantage of the invention comes from the use of gaseous oxygen found in air. While costly oxidants such as hydrogen peroxide or ozone are required in some of the current desulfurisation processes, the present process only requires the use of air as oxidant. Since air is abundant and freely obtainable from the atmosphere, the present process can be carried out very economically. The use of air also eliminates the need to carry out any oxidant recovery process that is usually required if liquid oxidants such as hydrogen peroxide are used. Another advantage of the inventive process comes from treating fuel in liquid phase, which allows mild process conditions (low process temperatures and pressures) to be used for the efficient oxidation of sulfur compounds, as compared to other desulfurisation processes known in the art in which more severe conditions are needed. Mild process conditions also mean that energy consumption for the process is low, thus resulting in further cost savings. Yet another advantage of the present invention is the ease of integration into any existing refinery for the production of diesel, as afforded by the mild process conditions of liquid phase contacting and the use of air. Furthermore, the use of a selective oxidation catalyst also permits the tuning of experimental parameters such as temperature and contacting time to achieve optimal conversion and selectivity. Conversions as high as 95% have been achieved in the present invention.

[0020] The present process is suitable for processing fuels having sulfur content ranging from several hundred to several thousand parts per million (ppm) by weight, effectively reducing the sulfur content to less than 100ppm. Sulfur content of a fuel that is to be treated may vary, depending for example on the geographical location from which the original crude oil is obtained, as

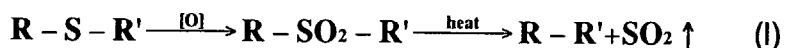
well as the type of fuel treated (e.g. whether the fuel is cracked or straight run). Depending on the sulfur level of the fuel to be treated, the present invention is sufficiently versatile to be implemented as a primary desulfurisation process or as a secondary desulfurisation process for treating
5 fuels. Non-limiting examples of fuels which can be treated by this invention include gasoline, kerosene, diesel, jet fuel, furnace oils, lube oils and residual oils. Additionally, the fuels that can be processed are not limited to straight-run fractions, i.e. fractions obtained directly from atmospheric or vacuum distillation in refineries, but include cracked fuels and residues which are
10 obtained from catalytic cracking of heavy crude oil fractions. As a primary desulfurisation unit, the invention can substitute conventional HDS processes to process straight-run fuels which typically have high sulfur content of several thousand ppm, even up to 10000 ppm (1%) or more. As a secondary desulfurisation unit, the present invention can be used for treating fuels that
15 have been undergone HDS treatment and thus have sulfur content of 500 ppm or less. In one embodiment, HDS is first carried out to lower sulfur content to the range of about 300 to 800 ppm. Thereafter, the process of the present invention can be used to further lower sulfur content to less than 100 ppm or even less than 50 ppm, if desired. For economic reasons, the initial
20 removal of high levels of sulfur from fuel is more suitably carried out by a conventional HDS process. In one embodiment, the fuel comprises diesel that has been treated in a hydrodesulfurization (HDS) process. In general, the present process is most preferably used for processing low viscosity fuels such as diesel and other fuels having viscosities that are comparable or lower
25 than diesel. Nevertheless, if required, this process can still be applied to heavier fractions such as lube oils and residual oils.

[0021] In the context of the invention, the term 'lowered sulfur content' refers to fuel that has sulfur content of less than 500 ppm by weight. The present invention is able to reduce sulfur content in fuels to less than 500
30 ppm, preferably less than 200 ppm, and more preferably less than 100 ppm, and most preferably less than 50 ppm.

[0022] Sulfur-containing compounds that are typically found in petroleum fractions and which can be removed by the process of the invention include aliphatic or aromatic sulfur-containing compounds such as sulfides (e.g. diphenylsulfide, dibutylsulfide, methylphenylsulfide), disulfides, and mercaptans, as well as heterocyclic sulfur-containing compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT), 4-methyl-dibenzothiophene (mDBT), 4,6-dimethyl-dibenzothiophene (dmDBT) and tribenzothiophene, and other derivatives thereof, for example.

[0023] The oxidation of the above sulfur-containing compounds occur at varying degrees of ease. Simple sulfur-containing compounds such as aliphatic or aromatic mercaptans and sulfides are generally more easily oxidized than heterocyclic sulfur-containing compounds. Heterocyclic compounds typically comprise thiophenic substances such as thiophenes, BT, DBT, alkylated DBTs such as 4-methyl-dibenzothiophene, 4,6-dimethyl-dibenzothiophene as well as other higher boiling point derivatives. One possible reason for the resistance to oxidation in the latter class of sulfur-containing compounds is the shielding of the sulfur by bulky hydrocarbon structures in the molecule. This class of sulfur-containing compounds are not easily oxidised or decoupled from the hydrocarbons by means of conventional HDS processes, and have thus become known as 'hard' or 'refractory' sulfur compounds.

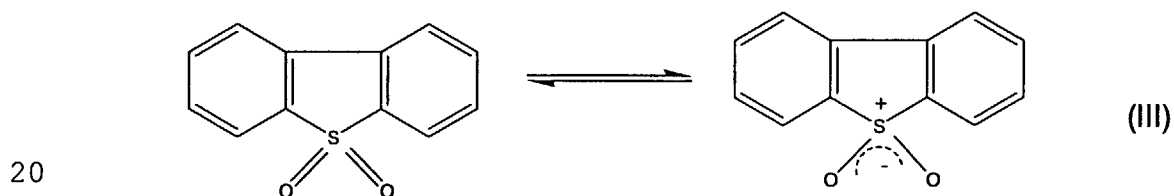
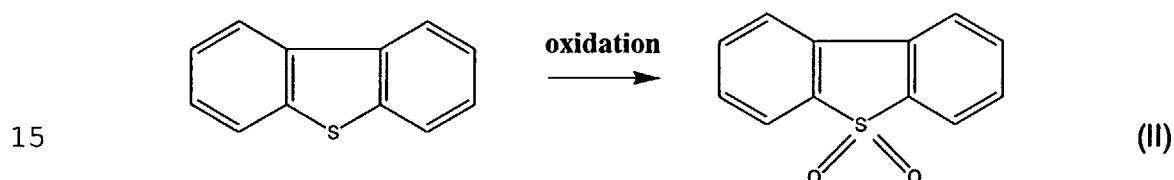
[0024] The conversion of thiophenic compounds into polar sulfones and/or sulfoxides using air as oxidant is the principal reaction carried out in the invention. The general reaction scheme for the ODS process is as follows:



As can be seen from scheme (I), the sulfones can decompose to liberate SO₂, while leaving behind a useful hydrocarbon compounds that can be utilised.

[0025] Air is utilised in the present invention to oxidise the residual sulfur compounds mainly into their corresponding sulfones. While it is

theoretically possible that some of the thiophenic sulfur compounds may be converted into other oxidised forms than sulfones, e.g. sulfoxides, gas chromatography data obtained from experiments according to the examples reveal that virtually no other sulfur compounds were formed. Without wishing to be bound by theory, it is believed that the sulfoxide species is unstable and will be oxidised into a corresponding sulfone by the process of the present invention. Accordingly, the present invention can be employed to convert sulfur compounds in fuels almost completely into sulfones, which can subsequently be extracted in a convenient manner. The oxidation of specific sulfur-containing compounds, particularly thiophenic compounds such as BT and DBT, which the present invention is effective in carrying out, is shown in the following illustrative reaction schemes:



It can be seen from the reversible scheme (III) that the S=O bonds can be polarised due to the loss of an electron from the sulfur atom to the pair of electronegative double-bonded oxygen atoms. It is probable that these polar compounds do not exist in a single form, i.e. either as a non-polarised sulfone or a fully polarised compounds, but rather as compounds having an intermediate range of dipole moment values. As most of the other liquid phase components in the reaction mixture are non-polar in nature, the polar sulfone compounds can be easily separated using conventional separation methods such as solvent extraction or adsorption.

[0026] The contacting of fuel with air can typically be carried out in any suitable continuous flow or batch reactor. Suitable continuous-flow reactors can, for example, be any commercially available tubular or packed-bed column reactor. Typical single fixed bed catalyst packing configurations found in hydrodesulfurisation processes can be used in the present invention. In order to provide uniform distribution of the catalyst in the reactor (thereby ensuring uniform temperature profile and gas pressure drop through the catalyst with no hot spots), the transition metal oxide catalyst can be held in any commercially available structured packing that can improve contact between the fuel, air and the metal oxide catalyst. The treated fuel leaving the ODS reactor contains both desulfurised fuel and oxidised sulfur compounds which can be readily separated by means of any suitable separation process such as solvent extraction or distillation. If a batch reactor is used, a fixed amount of fuel can be placed in the batch reactor while air is bubbled into the fuel. Once the reaction is complete, the oxidised sulfur compounds may be separated from the treated fuel using any suitable separation technique. If desired, treated fuel may be processed in a second run of the oxidation process to further reduce sulfur content in the fuel.

[0027] Generally, the contacting of fuel with air is carried out at a temperature range of between 90°C to 250°C, more preferably from 90°C to 200°C. The choice of the reaction temperature is typically influenced by factors such as the boiling range of the fuel being treated and the desired level of conversion. The boiling point of fuels that can be processed typically range from less than 100°C to several hundred degrees Celsius. For example, if the boiling range of the fuel is above 180°C, a reaction temperature range of 130°C to 180°C is used. Fuels having such a boiling range include kerosene, diesel, gas oil and heavy gas oils. As noted above, one advantage of the present invention is that the treatment of fuel takes place in the liquid phase, meaning that the contacting generally takes place at temperatures lower than the boiling range of the fuel for a given reaction pressure. It is known that an elevated reaction temperature is desirable for improving the kinetics of the

oxidation reaction, thereby obtaining higher conversion levels. However, due to the exothermicity of the oxidation reaction, high temperatures can be inhibitory from a thermodynamic viewpoint. Furthermore, an elevated temperature is associated with unwanted side reactions that can result in the formation of undesirable polymers and coke. Accordingly, an optimal reaction temperature range that takes into consideration these opposing factors would be beneficial in carrying out the invention.

[0028] In one embodiment, the contacting of fuel with air is carried out at a temperature range of about 110°C to 190°C, and preferably between 130°C and 180°C, and more preferably between 130°C to 160°C. A particularly preferred temperature range is between 130°C and 150°C, including about 130°C to 140°C, or even more preferably about 140°C. Accordingly, in some particularly preferred embodiments in which diesel fuel is treated and supported cobalt or manganese oxide catalysts are used, a preferred reaction temperature is about 150°C. In another particularly preferred embodiment, a preferred reaction temperature is about 130°C.

[0029] The pressure at which contacting is carried out should generally be low, but at the same time sufficiently high to avoid flashing of the fuel in the reactor that is lost with the effluent air. In general, reaction pressures that are typically used in the invention may be about 1 bar or may range from less than 1 bar to slightly above 1 bar (about 1.2 bar) or about 2.5 bars or about 5 bars. Carrying out the oxidation reaction at elevated reaction pressures may be advantageous as the elevated pressure may improve the oxidant concentration in the reaction system. In a preferred embodiment, the contacting takes place at ambient pressure, meaning at about 1 bar.

[0030] Notwithstanding the fact that certain temperatures ranges and pressures are preferred in specific embodiments, it should be noted that in the broad practice of the invention, the oxidation of sulfur containing compounds present in fuel can be achieved even if reaction temperatures and pressures falling outside the above preferred ranges are used, though the conversion rate may not be optimal in such cases.

[0031] The oxidation reaction which is carried out in the present invention involves the use of air as the (sole) oxidant for carrying out the oxidation of sulfur-containing compounds in the fuel. It is noted that the term "air" as used herein is to be understood in its regular meaning. The term thus
5 refers to a mixture of atmospheric gases comprising gases such as nitrogen, oxygen, carbon dioxide, trace amounts of other gases and optionally also water vapour. Gaseous oxygen is involved in the oxidation of the sulfur-containing compounds, while other gases such as nitrogen passes through the reactor without being involved in any reaction, given the mild reacting
10 conditions of the process. In this respect, the oxygen content in air is typically known to be about 21% by volume, although this level of oxygen may vary. Accordingly, the oxygen content of air that is used here may be at about its regular level in the atmosphere, i.e. 21%. It may, however, also be lower, e.g. if oxygen depleted air is used, or may be higher, if oxygen enriched air is
15 used. Depending of the oxygen level, the flowrate of air into the reaction environment can be adjusted dynamically by implementing a conventional feedback control, based for example based on the measured oxygen content of the air introduced into the reactor. Alternatively, instead of adjusting the flowrate of air into the reaction environment, the reaction environment can be
20 dynamically supplemented with a high purity oxygen stream using a feedback control.

[0032] The present invention makes use of a transition metal oxide catalyst for the oxidation of the sulfur-containing compounds. In the present invention, any transition metal oxide exhibiting catalytic activity towards the
25 oxidation of sulfur compounds, preferably hard sulfur compounds such as thiophenic compounds and the higher homologs thereof, may be used in the invention. Examples of suitable catalytic transition metal oxides include but is not limited to oxides of transition metals such as vanadium, chromium, manganese, cobalt, nickel, zirconium, niobium, molybdenum, rhenium,
30 tantalum, and tungsten. Specific examples of transition metal oxides include MnO_2 , Cr_2O_3 , V_2O_5 , NiO_2 , MoO_3 and Co_3O_4 . Chromates, vanadates,

manganates, rhenates, molybdates and niobates of the transition metal may also be used as catalyst. Depending on factors such as cost and availability, preferred transition metal oxides are those that exhibit highly catalytic activity towards the selective oxidation of sulfur containing compounds, especially thiophenic compounds.

[0033] In one embodiment, the transition metal oxide is an oxide of a metal selected from Groups 6, 7, 8 or 9 of the Periodic Table (IUPAC 1990), with oxides of manganese, cobalt, iron and chromium being presently preferred in the invention. In addition, the catalyst may comprise a single transition metal oxide or a mixture of transition metal oxides. The transition metal oxide catalyst can be present in a single or in multiple oxidation states.

[0034] Solid catalysts are preferably used in the invention. The catalyst can be present in any useable form, such as powders, pellets, extruded structures, monoliths or crushed structures, for example. Conventional techniques can be used prepare the catalysts in the desired form for use in the present invention. For example, in order to prepare powder catalysts, it is possible to calcine the corresponding metal nitrates or metal acetates under static air for 3 hours, using a calcination temperature in the range of 500 - 600°C in order to obtain the metal oxides. The heating rate can be pre-determined by thermal gravimetric analysis.

[0035] In certain embodiments of the invention, solid catalysts are preferably employed in the form of porous pellets. Porous catalyst pellets are commonly known and can be produced according to any conventional method. For example, it is possible to mix the catalyst components into a paste and extrude the paste as pellets, which are then baked at a high temperature. In order to obtain supported catalysts, it is possible to dope a support pellet with the transition metal oxide catalyst by immersing the support pellet in a salt solution of the transition metal. Additionally, pellets can adopt any suitable shape, including pellets that are spherical, cylindrical, star shaped or ring shaped, for example.

[0036] In one embodiment of the invention, the catalyst used is mounted/supported on a porous support. Supported catalysts are typically porous pellets having catalytic material deposited as a thin film onto its surface. The porous support can comprise a chemically inert material having
5 no effect on the oxidation reaction, or it can comprise a material that exerts a promoting effect on the catalyst which it supports, thereby improving the oxidation ability of the catalyst, e.g. silica carrier promotes chromia catalyst. Whilst catalyst pellets can comprise solely of catalytic material, it is usually not economically attractive since a substantial mass of catalytic material remains
10 locked within the pellet and is thus not effectively exposed for contact with reactants.

[0037] The use of a porous support helps to increase the surface area to volume ratio of the supported catalyst, thus providing a larger surface area for the oxidation reaction to take place. For this purpose, any variety of porous
15 support may be used, including microporous ($d < 2\text{nm}$), mesoporous ($2 < d < 50\text{nm}$) and macroporous ($d < 50\text{nm}$) supports. Materials which can be used as the porous support include metal oxides such as titania, alumina, ceria, magnesia, zirconia and tin oxide. Refractory materials that can withstand high reaction temperatures, such as ceramic materials, can also be
20 used, and examples include silica or alumina based ceramic materials. Other suitable materials include activated carbon, as well as members of the zeolite mineral group, for instance Y-zeolites, mordenite, clinoptilolite, chabazite, and phillipsite. It is presently possible that the support comprises one single material or a mixture or combination of several materials, such as amorphous
25 silica-alumina.

[0038] In one embodiment in which manganese and/or cobalt oxide is used as the catalytic material, the support comprises aluminium oxide (alumina), preferably γ -alumina. Alumina supports can be in the form of pellets or extrudates, and can be obtained by any conventional method, such as drop
30 coagulation of an alumina suspension, or via agglomeration.

[0039] Specific combinations of catalyst and support that are suitable for use in the invention include CoO/Al₂O₃, Co₃O₄/Al₂O₃, MnO₂/Al₂O₃, Mn₂O₃/Al₂O₃, CoO;Co₃O₄/Al₂O₃, Co₃O₄;MnO₂/Al₂O₃, CoO;MnO₂/Al₂O₃, CoO/SiO₂, Co₃O₄/SiO₂, MnO₂/SiO₂, Mn₂O₃/SiO₂, CoO;Co₃O₄/SiO₂,
5 Co₃O₄;MnO₂/SiO₂, CoO;MnO₂/SiO₂, MoO₂/Al₂O₃, MoO₃/Al₂O₃, Ru/SiO₂, Mg;Al/SiO₂, Co;Al/SiO₂, Ni/SiO₂, or Co;Ni/Al₂O₃, for example.

[0040] Apart from the selection of transition metal oxides to use as the catalyst, the choice of a suitable catalyst loading level can help to contribute to achieving an optimal oxidation of the sulfur-containing compounds. In this
10 context, catalyst loading is defined as the weight percentage of transition metal oxide present with respect to the support, preferably with respect to the weight of the support before loading the support with the catalyst. Generally speaking, catalyst loading can be determined once calcination has been carried out on the catalyst in which the transition metal salt is converted into
15 the corresponding transition metal oxide. For the ease of calculation of the catalyst loading, it is assumed in the present invention that the respective metal will be present after calcination as a homogenous oxide with a uniform oxidation state, for example as MnO₂, NiO₂, or Co₃O₄. Inductively coupled plasma spectroscopy (ICP) measurements can be made to determine the
20 metal concentration in the catalysts. From that ICP measurements, the actual percentage of the metal oxide present can be calculated. Apart from ICP, the prepared catalysts can also be analysed by Scanning Electron Microscopy (SEM) energy dispersive analysis by X-Ray (EDAX), which will give the surface composition of the catalyst. Loading levels that fall below the optimal
25 range (which can be determined empirically by the skilled person), may result in lower yields, while loading levels that are increased above the empirically determined optimal range may provide diminishing returns in terms of conversion. In one embodiment of the invention, the catalyst loading is in the range of 1 to 17%, more preferably between 2 to 13%, of the weight of the
30 support used. It should be noted that other catalyst loading values falling outside this range can nevertheless be used, even though they may be less

than optimal and may thus place compensatory demands on other areas of the process. For example, if a low loading level is used, the corresponding low conversion of the sulfur-containing compounds may necessitate higher space time, temperature or pressure, consequently leading to increased reactor size or possible unwanted side reactions, respectively.

[0041] Where the catalysts used in the invention are to be mounted onto supports, any conventional impregnation method known in the art may be used to prepare the catalysts. Such methods include incipient wetness, adsorption, deposition and grafting. If the incipient wetness method is used, for example, a solution containing a salt of the catalytic transition metal is first prepared. The support on which the catalyst is to be mounted may be subjected to pre-drying at elevated temperatures overnight before impregnation. This drying step helps to remove the adsorbed moisture from the pores and to fully utilize the pores for efficient and uniform impregnation of the metal salt solution. The concentration of the salt solution is prepared according to the desired catalyst loading level. For example, in order to prepare a catalyst with a loading level of 5% MnO_2 supported on γ -alumina, that is 0.5g of MnO_2 on 10g γ -alumina, 10g of pre-dried γ -alumina can be impregnated in a solution containing 1.409g of Mn(II) acetate $\times 4\text{H}_2\text{O}$ (molecular weight 245.09) dissolved in 8.0 ml deionised water. As can be seen from this example, it is assumed for the calculation of the catalyst loading that the Mn salt is completely converted into MnO_2 during the subsequent calcination and that formation of mixed metal oxides such as MnAl_2O_4 can be neglected. The wetted support is subsequently left to dry. The drying may be carried out by baking the wetted supports in an oven to calcine the catalyst. Calcination of the metal salt leads to the formation of a layer of metal oxide on the support.

[0042] In order to form a catalyst comprising a homogeneous mixture of two or more transition metal oxides, it is possible to wet the support structures in a mixture containing the salts of two or more of the desired transition metals. On the other hand, if it is desired to disperse several layers

of different transition metal oxides on the support, the impregnation and baking steps can be sequentially performed with the salt solution of each respective transition metal. In this context, the salt that is used to prepare a salt solution is known as the catalyst precursor. Suitable precursors include

5 crystalline salts of the transition metal such as nitrates, chlorides, sulphates, bromides, iodides, phosphates, carbonates, as well as organic compounds of the metals, such as acetates, benzoates, acrylates and alkoxides. It should be noted that in order to form a solution using these salts, they should be water soluble or soluble in an organic solvent. Methods of preparing suitable

10 supported or bulk catalysts for use in the present invention are described in Example 1 as well as taught in WO 03/051798 and the references cited therein, for example.

[0043] It is also contemplated that the catalyst formulation can additionally include other components, such as promoters which can enhance

15 catalyst activity or prolong the process lifespan of the catalyst. It may also be desirable that the catalysts are presulfided before use.

[0044] The process of the present invention may be supplemented by other suitable pre- or post-treatment steps. For example, the fuel to be treated can be subjected to prior chemical or thermal treatment before it is contacted

20 with air. It is also possible to pre-heat the process air prior to introducing the air into the reactor. Once the contacting has been performed, it is also possible to carry out a variety post-processing steps, such as separation steps to separate the oxidised sulfur compounds from the fuel or to remove any sulfur dioxide gas from the exhaust air prior to releasing it into the

25 atmosphere.

[0045] In order to remove the oxidised sulfur compounds, of which a large percentage comprises sulfones, from the treated fuel, the polarity of the sulfone molecule is relied upon to extract the sulfones from the hydrocarbon organic phase into aqueous phase. Thus, one embodiment of the present

30 invention further comprises adding a polar organic solvent to the treated fuel after contacting with air, thereby extracting the oxidised sulfur-containing

compounds from the treated fuel, and separating the polar organic solvent and the oxidised sulfur-containing compounds from the treated fuel. This embodiment is based on liquid-liquid extraction using polar solvents that are insoluble in the hydrocarbon fuel. The choice of solvent is influenced by several factors, such as selectivity of the oxidised sulfur compounds in the solvent, density of the solvent, insolubility of the solvent in the treated fuel, and recoverability of the solvent. One factor to consider in choosing a solvent is the selectivity of the solvent towards the polar oxidised sulfur-containing compounds. Typically, organic compounds having high polarity, as observed from their Hildebrand's solubility parameter, are selective towards the solvation of the oxidised sulfur compounds. Selectivity of extraction is important because the extraction of valuable carbonyl and aromatic hydrocarbons from the fuel should be minimised. Apart from this consideration, the selected fuel should preferably also be one that is immiscible (partition coefficient) in the fuel and has a different density from the treated fuel, so that the fuel/solvent mixture can be easily separated by conventional means such as gravity separation or centrifugation. It may also be helpful to choose a solvent that has a boiling point that is different from the boiling point of the sulfones to be extracted, so that distillation can be readily carried out to separate the sulfones from the solvent subsequently.

[0046] Various types of equipment can be used for solvent extraction, and its selection can depend on factors such as cost, size of equipment or process throughput, for example. When carrying out large scale solvent extraction of the oxidised sulfur compounds, a single stage mixer-settlers can be used, or if better extraction is desired, multi-stage cascades may be used instead. Alternatively, sieve tray extraction towers may also be used.

[0047] In one embodiment of the extracting step, between about 1 to 4 parts by volume of fuel is contacted with about 1 part by volume of polar organic solvent. The quantity of solvent used in solvent extraction affects the extent of extraction. While increasing the quantity of solvent improves the extraction of the oxidised sulfur compounds from the fuel, this advantage is

counteracted by other considerations such as increased costs due to the larger amounts of solvent being used as well as increase in the scale of solvent recovery operations.

[0048] Numerous polar organic substances can be used for the solvent
5 extraction of the oxidised sulfur compounds. These include acetonitrile (AcN), dimethyl sulfoxide, N,N'-dimethyl-acetamide, N-methyl-pyrrolidinone, trimethylphosphate, hexamethylphosphoric amide, methanol (MeOH), ethanol, propanol, butanol, carbon disulfide, pyridine, propylene glycol, ethylene glycol or any mixture thereof etc. In one embodiment, the polar organic solvent
10 comprises N,N'-dimethyl-formamide (DMF), 1-methyl-2-pyrrolidone (NMP), acetone or any mixture thereof. The solvent can also be diluted with water, if desired.

[0049] In general, the polar organic solvent and the dissolved oxidised sulfur compounds can be separated from the fuel by gravity separation or
15 centrifuging. The organic solvent can subsequently be recovered using any conventional separation method, such as evaporation, distillation or chromatography, to recover the solvent for recycle. The desulphurised fuel can be further processed, such as by washing with water or adsorption using silica gel or alumina, to remove traces of the solvent. The fuel thus obtained
20 has sulfur-content of typically less than 100 ppm, or preferably less than 50 ppm.

[0050] In one embodiment of the invention, the treated fuel is contacted with a basic adsorbent. The basic adsorbents used herein should exhibit a tendency towards the preferential adsorption of any acidic species present in
25 the fuel. The contacting step in this embodiment can be advantageously carried out after the separation/extraction step to eliminate remaining traces of the sulfones in the fuel. As sulfones are weakly acidic in nature, the use of a basic adsorbent can remove them as well as other acidic impurities such as other sulfur-based or nitrogen-based impurities from the fuel. Examples of
30 such basic adsorbents include zeolites, activated carbon, and layered-double hydroxides (LDH). LDHs are preferably used in some embodiments and

examples of suitable LDHs include those based on the metals Mn, Co, Ni, Cr, Al, Mg, Cu, Zn and Zr coupled with exchangeable anions such as NO_3^- , CO_3^{2-} and/or Cl^- , for example. The adsorption process can be carried out in any suitable furnace reactor, such as in a continuous flow tube furnace with the adsorbent packed as a fixed bed. In order to regenerate the adsorbent, a base can be added to the adsorption column to regenerate the adsorbent. The overall recovery that can be achieved with a combination of solvent extraction and adsorption can be as high as 92%.

[0051] The invention will be further explained by the following non-limiting examples and the accompanying figures, in which:

[0052] Figure 1 shows the simplified process flowsheet of the oxidative desulfurisation (ODS) process according to the invention.

[0053] Figure 2 shows the process flowsheet of a specific embodiment of the ODS process according to the present invention. In this embodiment, ODS is carried out as a secondary desulfurisation process for fuels that have been treated by conventional HDS. The treated fuel is channelled to a stirred/mixing tank containing a solvent for removing the oxidised sulfur compounds. The fuel/solvent mixture is then channelled to a settler where the treated fuel is separated from the solvent.

[0054] Figure 3 shows another embodiment of the process shown in Figure 2, in which the treated fuel is further passed through basic adsorbent column for further removal of the remaining sulfur-containing (which is slightly acidic in nature) compounds in the fuel. The fuel passing out of the adsorption column is sulfur-free.

[0055] Figure 4 shows the results of the analysis of the prepared catalysts based on the Brunauer, Emmett and Teller (BET) method.

[0056] Figures 5A to 5D show the results of analysis carried out with a gas chromatography Flame Ionisation Detector (GC-FID) on model diesel before oxidation was carried out (a) and after oxidation was carried out using the present invention (b). After solvent extraction using NMP was performed,

the fuel and the solvent layers were each analysed. Figures (c) and (d) shows the analysis results of the n-tetradecane layer the NMP layer, respectively.

[0057] Figures 6A to 6H show the individual gas chromatograms of specific samples of treated model diesel. In the experiments carried out for the results shown in Figures 6A & B, the catalyst used was 5% MnO_2/γ -alumina. Treatment temperature was 130°C. Figure 6A shows the analysis result before treatment, while Figure 6B shows the analysis result after treatment. Figures 6C & 6D show the GC results of model diesel treated in the absence of catalyst at a temperature of 130 °C, before treatment and after 18 hours of treatment, respectively. No oxidation was observed. Figures 6E & 6F show the GC analysis results of model diesel treated with 5% MnO_2/γ -alumina catalyst at a temperature of 150 °C, before treatment and after 18 hours of treatment, respectively. Figure 6G & 6H show the GC analysis results of model diesel treated with 8% MnO_2/γ -alumina catalyst at a temp. 150 °C, before treatment and after 18 hours of treatment, respectively.

[0058] Figure 7 shows the conversion of DBT vs. time in model diesel at 130°C for manganese (■)- and cobalt (◆)-containing catalysts.

[0059] Figure 8A shows the gas chromatography-atomic emission detection (GC-AED) chromatogram of untreated real diesel used in the examples. Figure 8B shows a table of data from X-ray florescence (XFR) analysis of sulfur content in untreated diesel that has undergone only solvent extraction.

[0060] Figure 9 shows a table of data from XRF analysis of sulfur content in real diesel that has been treated with either Co_3O_4 or MnO_2 catalyst supported on γ -alumina, and solvent extraction carried out with AcN, DMF, NMP and methanol. Treatment temperature was about 130°C.

[0061] Figure 10 shows a table of data from XRF analysis of sulfur content in real diesel that has been treated with MnO_2 catalyst supported on γ -alumina, and single or multiple solvent extraction carried out with AcN, DMF, NMP and methanol. Treatment temperature was either 130°C or 150°C.

[0062] Figures 11A to 11C show sulfur AED chromatograms of treated samples marked with superscript 3Ci, 3Cii and 3Ciii in the table in Figure 10.

[0063] Figure 12 shows a table of data from XRF analysis of sulfur content in real diesel that has been treated with MnO_2 catalyst supported on γ -alumina. Comparisons can be made between the effectiveness of sulfur removal employing a single solvent extraction using NMP and without employing any solvent extraction step. Treatment temperature was at 150°C. The initial sulfur content of the real diesel was 440-454 ppm. Sulfur content measurements were taken by ASTM 2622 (Brucker XRF).

[0064] Figure 13 shows the graph of sulfur content in a treated fuel sample vs ratio of solvent to diesel fuel applied in the solvent extraction process. It will be noted that sulfur content is generally reduced as solvent to fuel ratio is increased.

Example 1 : Catalyst preparation and characterization

[0065] The catalysts to be prepared comprise transition metal oxides and porous support with high specific surface area have been prepared by impregnation using incipient wetness method. 10g of γ -alumina pellet (diameter = 3-4mm, length = 6-10 mm, specific surface area = 370 m^2/g , specific pore volume ranged from 0.82ml/g to 0.87ml/g) was impregnated with cobalt nitrate and/or manganese acetate aqueous solutions. The total metal oxides loading with respect to γ -alumina ranged from 2 to 13 wt%. The impregnated sample was left on the roller which was set at 25 rpm for approximately 18 h to obtain better dispersion. The sample was then dried at 120°C in the oven for 18 h for removal of the water content. The dried sample was calcined in a static furnace at 550°C for 5 hours with a ramp of 5°C/min. Powder X-ray diffraction (XRD) showed that the catalysts were amorphous and that no distinguishable crystallographic properties could be observed among the catalysts. The prepared catalysts were also characterised by N_2 adsorption/desorption, and thermogravimetric analysis (TGA) in order to obtain the information on surface area, pore size distribution and pore volume,

crystallography and thermal decomposition of the samples. The BET method of measurement were used to determine the catalyst surface area. The characterisation data for the prepared catalysts used in the subsequent examples are summed up in the table in Figure 4.

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Example 2: Oxidative desulfurisation with solvent extraction using a model diesel

[0066] DBT and/or 4-MDBT were chosen to prepare model diesel by dissolving them in n-tetradecane with a total sulphur content of 500-800 ppm. In most of the experiments, sulfur content in the model diesel was introduced by adding only DBT. In the remaining experiments, both 4-MDBT and DBT were added. The oxidation experiments were carried out in a stirred batch reactor.

[0067] In a two-necked round bottom flask, 10.0 ml of model diesel containing approximately 500 ppm of sulphur underwent oxidative reaction in the presence of 20-30 mg of the catalyst (diameter = 3-4 mm, length = 6-10 mm). The mixture was magnetically stirred to ensure a good mixing and bubbled with purified air at flow of 60 ml/min. The reactions were carried out at a temperature range of 90 - 200°C. The optimum temperature for this specific set up was found to be 130°C at which the oxidation of the model compounds occurred successfully with insignificant side-reaction of solvent oxidation. A water-cooled reflux condenser was mounted on top of the reaction flask to prevent solvent loss and also function as an outlet for air.

[0068] At different time intervals (3h), 50 µl of the reacted diesel was withdrawn and diluted with 500 µl of diethylether for gas chromatography analysis. After the oxidation reaction, the oxidised products in the model diesel were extracted with polar organic solvents such as methanol, N,N-dimethylformamide (DMF), acetonitrile (AcN) and 1-methyl-2-pyrrolidone (NMP). During this process, the reacted model diesel was mixed with these polar organic solvents at different volume ratios (e.g. organic phase: polar solvent = 4:1 as shown in Fig. 5D) and was magnetically stirred vigorously for

1h. The mixture was then transferred into a separating funnel for the model diesel and polar organic solvent to be separated into different layers. The thus-treated model diesel was analysed with GC. The sulphur-containing polar solvent layer was then collected and analysed by GC. In the case of using
5 methanol, the methanol solvent was removed by the rotary evaporator. The remaining solid product was collected and analysed by the GC after re-dissolving into methanol or NMP (1-methyl-2-pyrrolidone) solvent.

[0069] Figures 5A to 5D shows the results of sulfur analysis from a gas chromatography-atomic emission detector (GC-FID) of the model diesel
10 before and after the oxidative process of the present invention carried out on model diesel. As shown in the results, almost complete conversion of DBT to the corresponding sulfone was achieved (cf. Figure 5A and 5B). A small percentage (about 5%) of n-tetradecane was oxidised to 6-tetradecanone, 2-tetradecanone and 4-tetradecanol. These are termed oxygenates and are
15 known to enhance diesel quality. It was found that NMP and DMF were better solvents than methanol and AcN. NMP solvent extraction achieved almost complete removal of the sulfones (cf. Figures 5C and 5D, in which a diesel:solvent volume ratio of about 4:1 was used). Additionally, multiple extractions were found to be better than a single extraction.

[0070] In a further experiment, specific samples of the model diesel
20 were treated with different MnO_2 catalysts having different catalyst loading levels, and at temperatures of either 130°C or 150°C. The treated diesel samples were analysed with gas chromatography (GC-FID) before the start of the oxidative treatment and after 18 hours of reaction time in order to
25 determine the catalytic activity of the catalyst for oxidation reaction using air as oxidant at 130 °C (Fig, 6A & 6B). In a similar experiment carried out without catalyst, it was observed that the reaction could not proceed (Fig. 6C & 6D). The result of the analysis are shown in Figures 6A to 6H. In summary, Figures 6A-6D show that the catalyst is important for the selective oxidation of
30 dibenzothiophene to corresponding sulfone at 130°C. Figures 6E- 6H further show that the catalytic activity of 5-8% MnO_2 loaded on gamma alumina for

model diesel and a reaction temperature of 150 °C provide advantageous conditions for selective oxidation of dibenzothiophene without oxidising the hydrocarbons such as tetradecane or pentadecane.

[0071] As can be seen from Figure 7 showing the conversion of DBT throughout the oxidative treatment, conversion reached above 90% between the reaction time of 15hr to 18hr.

Example 3: Oxidative desulfurisation and solvent extraction on real diesel

A) Solvent Extraction on Diesel Without Oxidative Treatment

[0072] Four 25.0 ml samples of untreated diesel was mixed with the polar organic solvents AcN, DMF, NMP and MeOH, respectively, in order to determine the effect of solvent extraction on sulfur compounds present in untreated fuel. After extraction by the respective polar solvents, the sulfur content of the diesel was measured by X-ray florescence (XRF). Untreated diesel had sulfur content of 370-380 ppm before extraction was carried out (measured by XRF using s-standard calibration curve). The GC-AED analysis of the sulfur content in the diesel is shown in Figure 8A. The results in Figure 8B show that among the solvents tested, NMP was most efficient in extracting sulfur compounds present in untreated fuel.

B) Oxidative Treatment using Co_3O_4 and MnO_2 catalysts supported on γ -alumina followed by solvent extraction

[0073] In a two-necked round flask, 100 ml real diesel underwent oxidative reaction in the presence of about 100 mg of catalyst. The mixture was magnetically stirred to ensure a good mixing and bubbled with purified air at flow of 60 ml/min. The reactions were carried out at 130°C. The reaction was stopped after about 18 hours. The oxidized diesel was cooled to room temperature and divided into four portions of 25ml each for extraction using different solvents (different volume). The analysis results are shown in Figure 9. Sulfur content of the extracted oxidized real diesel was measured by XRF

using s-standard calibration curve. Judging from this experiment, an 8% MnO₂ supported catalyst appeared to be more effective for removing sulfur from diesel than a 2% or 5% supported MnO₂ catalyst.

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C) Oxidative Treatment using MnO₂ catalysts supported on γ -alumina followed by single or multiple solvent extraction

[0074] In a two-necked round flask, 150 ml real diesel underwent oxidative reaction in the presence of about 30 mg of catalyst. The mixture was magnetically stirred to ensure a good mixing and bubbled with purified air at flow of 60 ml/min. The reactions were carried out at a temperature of either 130°C or 150°C. The reaction was stopped after about 18 hours. The oxidized diesel was cooled to room temperature and divided into five portions of 30 ml each for extraction using different solvents (different volume) via either single or multiple solvent extraction,

[0075] The analysis results are shown in Figure 10. Sulfur-content of the extracted oxidized real diesel was measured by XRF using s-standard calibration curve. Sulfur ppm levels indicated within the brackets () were measured using Antek 9000S (Singapore Catalyst Centre) ASTM D-5453 method. It can be seen that at a treatment temperature of 130°C, MnO₂ supported catalysts provided better sulfur removal at a loading level of 5% than at a loading level of 2%. Oxidative treatment carried out at a temperature of 150°C and using catalysts at a loading level of 8% provided better sulfur removal than treatments carried out at 130°C using catalysts having lower loading levels. Additionally, multiple solvent extractions were able to provide better sulfur removal than single solvent extractions.

[0076] Sulfur AED chromatograms were also obtained for specific treated samples (marked with superscript 3Ci, 3Cii and 3Ciii in the above figure) and are shown in Figures 11A to 11C.

30

D) Effect of solvent extraction on sulfur removal after carrying out oxidative treatment using MnO₂ catalysts supported on γ -alumina

5 **[0077]** In a two-necked round flask, 150 ml real diesel underwent oxidative reaction in the presence of various amounts of catalyst. The mixture was magnetically stirred to ensure good mixing and bubbled with purified air at flow of 60 ml/min. The reactions were carried out at 150°C for a period of about 24 hours. The oxidized diesel was cooled to room temperature and divided into five portions of 30 ml each. Each 30 ml portion was divided into two portions. One portion of each oxidized diesel sample was analysed after
10 oxidative treatment but prior to solvent extraction to determine the amount of SO₂ (gas) released during the oxidation process. The other portion of each of the samples underwent solvent extraction using 50 ml of a respective solvent. and then analysed for sulfur content (Bruker XRF using S-standardless method, ASTM 2622).

15 **[0078]** Based on the results shown in Figure 12, it can be seen that at a oxidation temperature of 150°C, sulfur removal provided by MnO₂ supported catalysts was most effective at a loading level of 8%, as compared to other loading levels of 5%, 11% or 13%.

WHAT IS CLAIMED IS:

1. A process for removing sulfur-containing compounds from fuel, said process comprising:
 - 5 contacting the fuel in liquid phase with air to oxidise the sulfur-containing compounds, said contacting being carried out in the presence of at least one transition metal oxide catalyst.
- 10 2. The process of Claims 1, wherein said contacting is carried out at a temperature range of between about 90°C to 250°C.
3. The process of Claim 1 or 2, wherein said contacting is carried out at a temperature range of between about 110°C to 190°C.
- 15 4. The process of any one of Claims 1 to 3, wherein said contacting is carried out at a temperature range of between about 130°C to 180°C.
5. The process of any one of Claims 1 to 4, wherein said contacting is carried out at a temperature range of between about 130°C to 160°C.
- 20 6. The process of any one of Claims 1 to 5, wherein said contacting is carried out at a pressure of about 1 bar.
7. The process of any one of Claims 1 to 6, wherein the catalyst is supported on a porous support.
- 25 8. The process of Claim 7, wherein the amount of catalyst supported on the porous support (catalyst loading) is in the range of about 1% to 17% by weight of the porous support.

9. The process of Claim 7, wherein the amount of catalyst supported on the porous support (catalyst loading) is in the range of 2% to 13% by weight of the porous support.
- 5 10. The process of any one of Claims 7 to 9, wherein the porous support comprises γ -alumina.
11. The process of any one of Claims 1 to 10, wherein the transition metal is selected from Groups 6, 7, 8 or 9 of the Periodic Table (IUPAC 1990).
- 10 12. The process of Claim 11, wherein the transition metal is selected from the group consisting of manganese, cobalt, iron, chromium and molybdenum.
13. The process of any one of Claims 1 to 12, further comprising:
- 15 adding a polar organic solvent to the treated fuel after contacting the fuel with air, thereby extracting the oxidised sulfur-containing compounds from the treated fuel, and
- separating the polar organic solvent and the oxidised sulfur-containing compounds from the treated fuel.
- 20 14. The process of Claim 13, wherein the polar organic solvent comprises acetonitrile, N,N'-dimethyl-acetamide, N-methyl-pyrrolidinone, trimethylphosphate, hexamethylphosphoric amide, methanol, ethanol, propanol, butanol, pyridine, propylene glycol, ethylene glycol, N,N'-
- 25 dimethyl-formamide, 1-methyl-2-pyrrolidone, acetone and mixtures thereof.
15. The process of Claim 13 or 14, wherein 1 part by volume of polar organic solvent is added to between about 1 to 4 parts by volume of treated fuel.
- 30 16. The process of any one of Claims 1 to 15, further comprising treating the treated fuel with a basic adsorbent.

17. The process of Claim 16, wherein the basic adsorbent is selected from the group consisting of zeolites, activated carbon, and layered-double hydroxides (LDH).
- 5
18. The process of Claim 16, further comprising washing the basic adsorbent with a basic solution to regenerate the basic adsorbent.
19. The process of any one of Claims 1 to 17, wherein the untreated fuel comprises sulfur content in the range of between about 300 to 800 ppm.
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20. The process of any one of Claims 1 to 18, wherein the fuel is diesel that has been treated in a hydro-desulfurisation process.
21. The process of any one of Claims 1 to 19, wherein the sulfur-containing compounds in the fuel comprise thiophenic compounds.
- 15
22. The process of Claim 20, wherein the thiophenic compounds are selected from the group consisting of thiophene, benzothiophene, dibenzothiophene, 4-methyl-dibenzothiophene, 4,6-dimethyl-dibenzothiophene and tribenzothiophene, and mono-, di-, tri-, and tetra-substituted compounds thereof.
- 20