

CATALYST SYSTEM AND USES

FIELD

The present disclosure relates to a catalyst system and its use in reducing the sulphur content of a hydrocarbon stream containing sulphur compounds, such as diesel. The present disclosure also relates to the recycling of the catalyst system in further desulphurisation processes.

BACKGROUND

Crude oil is primarily a mixture of hydrocarbons, typically paraffins (alkanes), naphthenes (cycloalkanes) and aromatics, with impurities such as heteroatom compounds (S, N, O), metals (e.g nickel, vanadium and iron), organic compounds and inorganic compounds such as sodium, calcium and chlorine. These impurities can impact on the processing requirements and the quality of products produced from the refining process. Heteroatoms such as sulphur require particular attention as clean fuel legislation places limits on the maximum level of sulphur in various petroleum products.

The burning of hydrocarbon fuels containing sulphur compounds results in oxidation of the sulphur compound during the combustion process to produce oxides of sulphur (SO_x). Sulphur oxides are known to contribute to environmental pollution, health issues, potential catalyst deactivation and equipment corrosion, amongst others effects. The removal or reduction of sulphur compounds from liquid hydrocarbon streams, such as crude oil and petroleum products including Natural Gas Condensate, Kerosene, Jet Fuel, Diesel and Fuel Oil, before they are combusted is important to minimise these detrimental effects and is ultimately required to comply with mandated global emissions standards.

Conventional hydrotreating processes remove organic sulphur containing compounds from fuel oils by hydrogenation. In addition to high investment and running costs, this process results in the production of toxic hydrogen sulphide gas.

The process of oxidative desulphurisation to remove sulphur from diesel and other oil streams utilises oxidants and catalysts which are both costly and usually contribute to high operating cost of the process. The operating costs and safety considerations of such

a process are dependent to a large extent on the cost of purchasing the chemical components that are consumed or not recycled and the potential hazards of the process. The global move to clean energy (green technology) and environmental consciousness has placed an increasing focus on the efficient use of catalysts and oxidants in such a process.

There is a need to develop new technologies for the desulphurisation of hydrocarbon streams that are commercially viable. There is a need to remove impurities from hydrocarbon streams such as crude oil. There is a need for an alternate and/or improved process for the oxidative desulphurisation of hydrocarbon streams. There is also a need for an alternate and/or improved catalyst that is effective in a process of oxidatively desulphurising a hydrocarbon streams. There is also a need for alternate catalysts that allow the oxidative desulphurisation process to be carried out in a manner that is efficient, cost effective, safety conscious and/or environmentally considerate.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present disclosure as it existed before the priority date of each of the appended claims.

SUMMARY

The present inventors have undertaken significant research into identifying and developing a catalyst system that is economical, environmentally aligned, effective and surprisingly highly active when used in a process of removing sulphur compounds from hydrocarbon material containing sulphur, such as diesel and fuel oil.

Disclosed herein is a method of preparing a catalyst system comprising combining one or more phase transfer catalysts (PTC); one or more metal oxides; one or more oxidants; and one or more inorganic acids, wherein the method does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture. In one embodiment, the method comprises combining one or more phase transfer catalysts (PTC); one or more metal oxides; an oxidant; and one or more inorganic acids,

wherein the method does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

In one aspect, there is provided a method of preparing a catalyst system, the method comprising combining one or more phase transfer catalysts (PTC) and one or more metal oxides; followed by addition of one or more oxidants and one or more inorganic acids. In one embodiment, there is provided a method of preparing a catalyst system, the method comprising combining one or more phase transfer catalysts (PTC) and one or more metal oxides; followed by addition of an oxidant and one or more inorganic acids. In one embodiment, there is provided a method of preparing a catalyst system, the method comprising combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid.

The oxidant may be added in the last step or in the penultimate step.

In one embodiment, the oxidant is added last. Accordingly, in one embodiment, the method comprises combining the phase transfer catalyst (PTC) and one or more metal oxides; adding the inorganic acid; followed by addition of the oxidant.

In another embodiment, the inorganic acid is added last. Accordingly, in one embodiment, the method comprises combining the phase transfer catalyst (PTC), one or more metal oxides; adding the oxidant; followed by addition of the inorganic acid.

In another aspect, there is provided a method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by addition of an inorganic acid. Said another way, in this embodiment, the method comprises i) contacting the oxidant with a mixture comprising the phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by ii) adding the inorganic acid to the mixture formed in i).

In one embodiment, the method comprises combining the phase transfer catalyst (PTC) and one or more metal oxides; adding the oxidant, followed by addition of the inorganic acid.

In another aspect, there is provided a method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC); one or more metal oxides; and an inorganic acid.

In one embodiment, the method comprises combining the phase transfer catalyst (PTC), one or more metal oxides and the inorganic acid; followed by addition of the oxidant.

5 In one embodiment, the one or more metal oxides is combined with the PTC prior to combining with the inorganic acid. In one embodiment, the one or more metal oxides is added to the PTC. In one embodiment, the PTC is added to the one or more metal oxides.

10 In one embodiment, the method comprises: a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC; b) adding the inorganic acid to the mixture of metal oxide and PTC followed by: c) addition of the oxidant.

In one embodiment, the method comprises: a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC; b) adding the oxidant to the mixture of metal oxide and PTC followed by: c) addition of the inorganic acid.

15 In another aspect, there is provided a method of preparing a catalyst system comprises combining a PTC and oxidant to form a mixture of PTC and oxidant, adding the metal oxide to the mixture of PTC and oxidant, followed by adding the inorganic acid.

20 In another aspect, there is provided a method of preparing a catalyst system, the method comprising the steps of: a) combining sodium tungstate dihydrate and an aqueous quaternary ammonium salt to form a metal oxide and quaternary ammonium salt mixture; b) adding aqueous phosphoric acid to the metal oxide and quaternary ammonium salt mixture to form a reaction mixture; followed by c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst mixture; d) allowing the oxidised catalyst mixture to settle to form multiple layers including a water immiscible layer containing the catalyst system; and d) optionally separating the water immiscible layer containing the catalyst system.

25 Also disclosed herein, is a catalyst system prepared by combining one or more phase transfer catalyst (PTC); one or more metal oxides; one or more oxidants; and one or more inorganic acids wherein the preparation does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

In one aspect, there is provided a catalyst system prepared by combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid(s).

5 In one embodiment, the oxidant is added last. In another embodiment, the inorganic acid is added last.

In another aspect, there is provided a catalyst system prepared by contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC); one or more metal oxides; and an inorganic acid(s).

10 In one embodiment, the catalyst system is prepared by contacting aqueous hydrogen peroxide with a solution comprising a quaternary ammonium salt; sodium tungstate dihydrate; and aqueous phosphoric acid.

In another aspect, there is provided a catalyst system prepared by contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an inorganic acid(s).

15 In one embodiment the one or more metal oxide(s) is first contacted with the one or more quaternary ammonium salt(s).

In one embodiment the solution is prepared by mixing the metal oxide with the quaternary ammonium salt and subsequent contact with the inorganic acid.

20 In one embodiment a Group VIb metal oxide is first contacted with phosphoric acid followed by addition of a quaternary ammonium salt, followed by addition of oxidant.

25 In another aspect, there is provided a catalyst system prepared by contacting an oxidant with a phase transfer catalyst (PTC) to form a mixture of PTC and oxidant; and adding to the mixture one or more metal oxides and an inorganic acid(s). In one embodiment, the one or more metal oxides is added to the mixture followed by addition of the inorganic acid.

30 In another aspect, there is provided a process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds, the process comprising: a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system prepared by the method disclosed herein, so as to oxidise at least a portion of the sulphur compounds in the hydrocarbon material to form an

oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and b) separating at least a portion of the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with reduced sulphur content.

In another aspect, there is provided a process of recycling the catalyst system used
5 in the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds disclosed herein.

In one embodiment the process of recycling the catalyst system comprises: a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system to form an oxidised hydrocarbon mixture comprising
10 oxidised sulphur compounds; b) allowing the oxidised hydrocarbon mixture to settle to form a layer containing the catalyst system; and c) separating the catalyst system as a recovered catalyst system and recycling the recovered catalyst system by contacting the recovered catalyst system in the presence of hydrogen peroxide with a further hydrocarbon material containing sulphur compounds, for a period of time sufficient to
15 oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture.

In one embodiment the process of recycling the catalyst system comprises: a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system for a period of time to oxidize at least a portion of the
20 sulphur compounds to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; b) allowing the oxidised hydrocarbon mixture to settle for a sufficient period of time to form three layers: i) an aqueous layer, ii) a hydrocarbon layer comprising oxidised sulphur compounds, and iii) a layer containing the catalyst system; and c) separating the layer containing the catalyst system as a recovered catalyst system
25 and recycling the recovered catalyst system by contacting the recovered catalyst system in the presence of hydrogen peroxide with a further hydrocarbon material containing sulphur compounds, for a period of time sufficient to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture.

In another aspect, there is provided a hydrocarbon material obtainable from the
30 process for reducing the sulphur content of a hydrocarbon material containing sulphur compounds as disclosed herein.

In another aspect, there is provided a hydrocarbon material obtainable from the process for reducing the sulphur content of a hydrocarbon material containing sulphur compounds as disclosed herein, wherein sulphone and/or sulfoxide compounds are present in the extractant used in the process.

5 In another aspect there is provided an apparatus for reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to the process disclosed herein, the apparatus comprising: a) one or more oxidation reactors for oxidising at least a portion of the sulphur compounds in the hydrocarbon material containing sulphur in the presence of the hydrogen peroxide and the catalyst system
10 disclosed herein, to provide the oxidised hydrocarbon mixture comprising hydrocarbon material, oxidised sulphur compounds, and catalyst system; b) one or more vessels for delivering the hydrogen peroxide and the catalyst system to the oxidation reactor; c) a means for separating the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with reduced sulphur content; d) a means for
15 separating the hydrocarbon stream with reduced sulphur content; e) a means for separating the catalyst system; f) one or more mixers for mixing the hydrocarbon material with reduced sulphur content with an extraction solvent to extract oxidised sulphur compounds into the extractant and g) means to separate the hydrocarbon material with reduced sulphur content.

20 In some embodiments, the catalyst system is recycled as a recovered catalyst system and the apparatus further comprises a means for storing the recovered catalyst system for further use in the process for reducing the sulphur content in a hydrocarbon material as described herein.

According to at least one embodiment of the process disclosed herein, the present
25 inventors have surprisingly found a unique methodology of forming a highly reactive catalyst system that can be used at greatly reduced catalyst loading levels while achieving efficient oxidative desulphurization of a hydrocarbon material.

In one embodiment, the methodology involves forming the catalyst system by adding the oxidant (e.g. hydrogen peroxide) last or in the penultimate step to a mixture
30 comprising a phase transfer catalyst (PTC) (e.g. quaternary ammonium hydrogen sulphate), a metal oxide (e.g. sodium tungstate) and an inorganic acid (e.g. phosphoric

acid). The inventors have unexpectedly found that the order of addition of the ingredients creates an activated catalyst for oxidative desulphurization that is more active than a catalyst prepared according to known methodologies.

5 In another embodiment, the methodology involves a step where the oxidant is combined with the PTC to form a mixture comprising the oxidant and the PTC which does not yet further comprise the metal oxide and/or inorganic acid.

The process of the present disclosure shows that the order of addition of the components to form the catalyst system results in drastic reduction in the level of expensive metal (e.g. tungsten) and significant reduction in the oxidant (e.g. hydrogen
10 peroxide) consumption. These two achievements are surprising in light of current methodology that uses these components in substantial excess. In one embodiment, the process disclosed herein greatly improves the cost, safety and/or environmental performance of the oxidative desulphurization process.

Advantageously, the process of reducing the sulphur content of a hydrocarbon
15 material containing sulphur compounds of the present disclosure reduces the usage and consumption amounts of the two most expensive components of the oxidative desulphurization process which are the transition metal(s) of the catalyst (most notably tungsten) and the oxidant (e.g. hydrogen peroxide) that is consumed.

In one or more embodiments, the present disclosure provides a catalyst system
20 that provides one or more benefits selected from: cost reduction for greatly enhanced economic viability, reduced materials management and higher safety performance and higher environmental performance, while maintaining the high levels of desulphurization that meet the highest standards and strictest requirements set by the authorities in all countries and international organizations that determine the regulations for sulphur levels
25 in hydrocarbon fuel.

Advantageously, the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds as described herein, also reduces the TAN (total acid number) of the hydrocarbon material.

It will be appreciated that other aspects, embodiments and examples of the
30 products and ingredients are described herein, along with preparation, methods and systems for production thereof.

FIGURES

Figure 1 shows a representative flow sheet of one embodiment of the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds.

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Figure 2 shows the sulphur content in ppm following oxidative desulphurisation of transmix diesel (with 280 ppm sulphur content) using the baseline catalyst prepared using prior art methodology.

10 Figure 3 shows the sulphur content in ppm following oxidative desulphurisation of transmix diesel (with 280 ppm sulphur content) using the catalyst system of the present invention.

Figure 4 shows the sulphur content in ppm following oxidative desulphurisation of transmix diesel (with 280 ppm sulphur content) using the catalyst system of the present invention compared to oxidative desulphurisation of transmix diesel using the baseline catalyst.

20 Figure 5 shows the sulphur content in ppm following oxidative desulphurisation of transmix diesel (with 280 ppm sulphur content) using the catalyst system of the present invention compared to oxidative desulphurisation of transmix diesel using the baseline catalyst.

25 Figure 6 shows the sulphur content in ppm following oxidative desulphurisation of transmix diesel (with 280 ppm sulphur content) using a recycled catalyst system of the present invention compared to oxidative desulphurisation of transmix diesel using the baseline catalyst.

DETAILED DESCRIPTION30 **Terms**

Unless specifically defined otherwise, all technical and scientific terms used herein shall be taken to have the same meaning as commonly understood by one of ordinary skill in the art (e.g., chemistry, chemical engineering, and the like).

35 Unless specifically stated otherwise, or the context requires otherwise, reference to a single step, composition of matter, group of steps or group of compositions of matter

shall be taken to encompass one and a plurality (i.e. one or more) of those steps, compositions of matter, groups of steps or groups of compositions of matter. Thus, as used herein, the singular forms "a", "an" and "the" include plural aspects unless the context clearly dictates otherwise. For example, reference to "a" includes a single as well
5 as two or more; reference to "an" includes a single as well as two or more; reference to "the" includes a single as well as two or more and so forth.

Those skilled in the art will appreciate that the disclosure herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the disclosure includes all such variations and modifications. The disclosure also
10 includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features.

Each example of the present disclosure described herein is to be applied mutatis mutandis to each and every other example unless specifically stated otherwise. The
15 present disclosure is not to be limited in scope by the specific examples described herein, which are intended for the purpose of exemplification only. Functionally-equivalent products, compositions and methods are clearly within the scope of the disclosure as described herein.

As used herein, the term "and/or", e.g., "X and/or Y" shall be understood to mean
20 either "X and Y" or "X or Y" and shall be taken to provide explicit support for both meanings or for either meaning, e.g. A and/or B includes the options: (i) A, (ii) B or (iii) A and B.

As used herein, the term about, unless stated to the contrary, refers to +/- 20%, typically +/- 10%, typically +/- 5%, of the designated value.

25 It is to be appreciated that certain features that are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination.

Throughout the present specification, various aspects and components of the
30 invention can be presented in a range format. The range format is included for convenience and should not be interpreted as an inflexible limitation on the scope of the

invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range, unless specifically indicated. For example, description of a range such as from 1 to 5 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 5, from 3 to 5 etc., as well as individual and partial numbers within the recited range, for example, 1, 2, 3, 4, 5, 5.5 and 6, unless where integers are required or implicit from context. This applies regardless of the breadth of the disclosed range. Where specific values are required, these will be indicated in the specification.

10 Throughout this specification the term "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

 As used herein the terms "combination" and "mixture" of ingredients may be used interchangeably.

15 As used herein the term "consisting essentially of" or "consists essentially of" refers to those elements required for a given embodiment. The term permits the presence of elements that do not materially affect the basic and novel or functional characteristic(s) of that embodiment of the invention. The term "consisting of" refers to methods, and respective components thereof as described herein, which are exclusive of any element not recited in that description of the embodiment.

20 As used herein, the phrase "at least one of", when used with a list of items, means different combinations of one or more of the listed items may be used and only one of the items in the list may be needed. The item may be a particular object, thing, or category. In other words, "at least one of" means any combination of items or number of items may be used from the list, but not all of the items in the list may be required. For example, "at least one of item A, item B, and item C" may mean item A; item A and item B; item B; item A, item B, and item C; or item B and item C. In some cases, "at least one of item A, item B, and item C" may mean, for example and without limitation, two of item A, one of item B, and ten of item C; four of item B and seven of item C; or some other suitable combination.

It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents forms part of the common general knowledge in the art, in Australia or in any other country.

5 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. In case of conflict, the present specification,
10 including definitions, will prevail. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

As used herein the term “sulphur compound” refers to a compound that contains one or more sulphur atoms, for example, compounds that contain -S-, -C-S-, -S-S-, -(S)_n- where n > 1, -C(=S)- and SH. In one embodiment, the sulphur compounds are
15 organically combined sulphur compounds (organosulphur compounds) including aliphatic and aromatic sulphur containing compounds such as sulphides (e.g. diphenylsulphide, dibutylsulphide, methylphenylsulphide), disulphides and mercaptans as well as heterocyclic sulphur-containing compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT), 4-methyl-dibenzothiophene (mDBT),
20 4,6-dimethyl-dibenzothiophene (DMDBT) and trimethyl-dibenzothiophene (TMDBT). In one embodiment, material containing sulphur compounds as defined herein, are capable of being removed from the material by the oxidative desulphurisation process disclosed herein.

“Oxidative desulphurisation” of a material containing sulphur compounds may be
25 carried out by known methodology and involves reacting the material containing sulphur compounds with an oxidising agent to form oxidised sulphur compounds which may be removed from the material by, for example, extraction or distillation.

As used herein, the term “oxidised sulphur compound” refers to a sulphur compound in an oxidised form, for example, in the form of a sulphone or sulfoxide.

As used herein the term "hydrocarbons" will be understood to mean organic compounds that contain only carbon and hydrogen and include aliphatic and aromatic hydrocarbons (alkanes, alkenes, alkynes and arenes).

As used herein the term "hydrocarbon material" will be understood to mean
5 material made up of aliphatic and/or aromatic hydrocarbons and/or olefinic hydrocarbons and includes crude oil and petroleum products such as Natural Gas Condensate, Kerosene, Jet Fuel, Diesel and Fuel Oil and hydrotreated diesel and fuel oil.

As used herein, the term TAN will be understood to mean "total acid number". Low quality crude oil is reflected by a high TAN. High TAN crude oils are acidic and
10 therefore are more difficult to process. Generally TAN in crude oil is caused by the presence of naphthenic acids. Naphthenic acid is used in a generic sense to refer to all of the carboxylic acids present in petroleum, whether cyclic, acyclic, or aromatic compounds, and carboxylic acids containing heteroatoms such as nitrogen and sulphur. The total acid number (or TAN) of a crude oil is a measure of the corrosiveness of the
15 crude oil due to the presence of acids, particularly naphthenic acids. As used herein, TAN is measured based on the mg of potassium hydroxide required to neutralize one gram of crude. Generally, a TAN greater than 1 is considered high for crude oil. The legislative limit for a finished product, such as diesel/marine gas oil, is 0.50mg KOH/g.

The term "hydrocarbon material containing sulphur compounds" will be
20 understood to mean hydrocarbon material as defined herein that contain sulphur compounds that is to be subject to the process disclosed herein to reduce the sulphur content. It may, hereinafter also be referred to as the "hydrocarbon feedstock", "feedstock" or "feed stream".

The term "hydrocarbon material with a reduced sulphur content", will be
25 understood to mean that the proportion of sulphur compounds in the hydrocarbon material is lower than the proportion of sulphur compounds in the "hydrocarbon material containing sulphur compounds" before contact with the oxidant and catalyst. In a preferred embodiment an "ultra low sulphur hydrocarbon" or "ULSD" material is produced having a sulphur content of less than 15 ppm by weight sulphur. In one
30 embodiment the USLD has a sulphur content of less than 10 ppm or 15 ppm by weight

of sulphur that is compliant with road transportation fuel requirements in Europe and US respectively.

It will be understood that the “hydrocarbon material with a reduced sulphur content” may contain sulfoxide and/or sulphone compounds in varying amounts depending on the degree of their removal following, for example, solvent extraction, and/or distillation.

The term “sulfoxide and/or sulphone stream” or “sulfoxide and/or sulphone containing material” and the like, will be understood to mean any amount of sulfoxide and/or sulphone obtained following solvent extraction of the oxidised hydrocarbon material. It will be appreciated that the “stream” or “material” obtained from a first extraction of an oxidised hydrocarbon material may contain more sulfoxide and/or sulphone than subsequent streams obtained following multiple extractions of the same oxidised hydrocarbon material.

As used herein, the term “sulfoxide” or “sulfoxide compound” will be understood to mean a compound that contains a $-S(=O)-$ group.

As used herein, the term “sulphone” or “sulphone compound” will be understood to mean a compound containing a sulphonyl group, i.e. a compound containing a $-S(=O)_2-$ group.

The term “desulphurising a hydrocarbon material” has the same meaning as “reducing the sulphur content in a hydrocarbon material” and the two terms may be used interchangeably. Similar phrases such as “desulphurised hydrocarbon material” and the like, will also be understood to have the same meaning as “hydrocarbon material with reduced sulphur content” and the like, and it will be understood that they can be used interchangeably.

The term “recovered catalyst system” as used herein refers to the post oxidative catalyst system that is recovered following the oxidative process.

As used herein, the term “halogen” means fluorine, chlorine, bromine, or iodine.

As used herein, term “alkyl” or “alkyl group” will be understood to mean a hydrocarbyl group that has the formula C_nH_{2n+1} . The term “alkyl” encompasses both straight-chain (i.e., linear) and branched-chain hydrocarbon groups. Examples of alkyl groups include, but are not limited to: methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-

butyl, i-butyl, sec-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl and nonadecyl groups.

The expression “C₁-C_n alkyl” refers to an alkyl group that has in the range of 1 to n carbon atoms (where n is positive integer). In one example, the alkyl group is in the range of one to ten carbon atoms which may be referred to as C₁₋₁₀alkyl or C1-C10 alkyl or C₁H₃- C₁₀H₂₁ alkyl. In one example, the alkyl group is a mixture of hydrocarbyl chains of eight and ten carbon atoms, which may be referred to as a C₈₋₁₀alkyl, C8-C10 alkyl or C₈H₁₇- C₁₀H₂₁ alkyl group.

As used herein, term “tetraalkylammonium group” or “tetraalkylammonium cation” will be understood to mean a central nitrogen atom bound to four alkyl groups. In one example, each of the alkyl groups is a C1-C10 alkyl. In one example the tetraalkylammonium group is a triC8-C10alkyl methyl ammonium cation. The term “triC8-C10alkyl methyl ammonium” refers to three alkyl groups, that independently represent an alkyl group that is either C₈H₁₇ or C₁₀H₂₁, and a methyl group that are all attached to a nitrogen atom.

As used herein, the term capryl group will be understood to mean the alkyl group C₈H₁₇ also known as octyl.

As used herein, the term caprylyl group will be understood to mean a mixture of octyl (C₈H₁₇) alkyl groups and decyl (C₁₀H₂₁) alkyl groups. In one embodiment, the molar ratio of octyl groups to decyl group is 2:1.

As used herein, the term “stearyl” group will be understood to mean an octadecyl group.

As used herein, the term “cetyl” group will be understood to mean an hexadecyl group.

As used herein, the term “hexaalkyl guanidinium” will be understood to mean di alkyl substitution at each of the three nitrogen atoms on the guanidine structure, wherein alkyl is as defined herein.

As used herein, the term “alkyl pyridinium” will be understood to mean alkyl substitution at the nitrogen atom in the pyridine structure, wherein alkyl is as defined herein.

As used herein, the term “phosphonium” will be understood to mean [1] alkyl substitution at the phosphorous atom to form a tetra substituted phosphonium cation, wherein alkyl is as defined herein or [2] alkyl triaryl phosphonium in which alkyl is defined herein and aryl is defined as phenyl or substituted phenyl or [3] tetraaryl phosphonium in which aryl is defined as phenyl or substituted phenyl.

As used herein, the term “raffinate” refers to a liquid from which impurities have been removed by solvent extraction.

As used herein the term “water immiscible” means a material (e.g. hydrocarbon) that forms two phase with water. It will be appreciated that a water immiscible layer may contain a small amount of water, either by molecular hydration or by occlusion/emulsion.

Product by process

Also disclosed herein is a catalyst system prepared by combining one or more phase transfer catalysts (PTC); one or more metal oxides; one or more oxidants; and one or more inorganic acid(s), wherein the preparation does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

In one aspect, the catalyst system is prepared by combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid(s).

In one aspect, the catalyst system is prepared by contacting an oxidant with a mixture comprising: a) a phase transfer catalyst (PTC); b) one or more metal oxides; and c) an inorganic acid(s).

In one aspect, the catalyst system is prepared by contacting an oxidant with a mixture comprising: a) a phase transfer catalyst (PTC); and b) one or more metal oxides; followed by addition of an inorganic acid(s).

In one embodiment, the catalyst system is prepared by contacting aqueous hydrogen peroxide with a solution comprising: a) a quaternary ammonium salt; b) sodium tungstate dihydrate); and c) aqueous phosphoric acid.

In one embodiment the one or more metal oxide(s) is first contacted with the one or more quaternary ammonium salt(s).

In one embodiment the solution is prepared by mixing the metal oxide with the quaternary ammonium salt and subsequent contact with the inorganic acid.

- 5 In another aspect, the catalyst system is prepared by combining the PTC and the oxidant to form a mixture of PTC and oxidant, adding the metal oxide to the mixture of PTC and oxidant, followed by adding the inorganic acid.

Catalyst System

- 10 The catalyst system disclosed herein combining one or more phase transfer catalysts (PTC), one or more metal oxides; one or more oxidants and one or more inorganic acids, wherein the preparation does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

- 15 In one aspect, the catalyst system disclosed herein is prepared by combining a phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by addition of an oxidant and an inorganic acid. The inorganic acid may be added to the PTC and metal oxide mixture followed by addition of the oxidant; or the oxidant may be added to the PTC and metal oxide mixture followed by addition of the inorganic acid.
- 20 Importantly, the method of preparing the catalyst system involves a specific order of addition of ingredients, with the oxidant and inorganic acid being added after the PTC and one or more metal oxides have been combined. The addition of the oxidant last or in the penultimate step in this method of preparation has been found to be important in producing the active catalyst system disclosed herein.

- 25 In another aspect, the catalyst system disclosed herein is prepared by combining phase transfer catalyst (PTC) and oxidant to form a mixture of PTC and oxidant, adding one or more metal oxides to the mixture of PTC and oxidant, followed by adding inorganic acid. Throughout the specification this preparation process may be referred to as “combining a PTC and oxidant followed by addition of a metal oxide and inorganic
- 30 acid”.

Without being bound by theory, the inventors believe the catalyst system prepared by the method disclosed herein, comprises a polyoxometallate (POM) which is highly oxygenated compared to POM's formed by prior art methodology. The prior art methodology, involves a mechanism of forming POM's wherein the addition of the oxidant occurs early in the preparation and the addition of the PTC occurs last, specifically, the prior art methodology (such as that disclosed in Example 1 of US8,715,489) involves the oxidant and metal oxide being combined before addition of the inorganic acid followed by addition of the PTC. The catalyst system disclosed herein is formed by a different order of addition which does not involve a step where the oxidant is combined with the metal oxide in isolation. In one embodiment of the present disclosure, the PTC is added to the metal oxide early in the preparation and the oxidant is added later. In another embodiment, the oxidant is combined with the PTC early in the preparation. It is believed that a different mechanistic pathway operates in the formation of a different POM. The inventors believe that the addition of the oxidant, such as hydrogen peroxide, at a different stage in the process as disclosed herein, such as later in the process, results in a highly oxygenated POM that is unusually highly active. In one embodiment, the catalyst system prepared according to the process disclosed herein is surprisingly reactive compared to catalysts prepared by other methodologies, particularly methodologies where the oxidant is combined directly with the metal oxide and not added in the order disclosed herein, such as later in the preparation of the catalyst.

Reaction mixture and oxidised catalyst mixture

The method of preparing the catalyst system disclosed herein comprises combining a phase transfer catalyst (PTC), one or more metal oxide oxides; an oxidant and an inorganic acid, wherein the method does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

In one aspect, the method of preparing the catalyst system disclosed herein comprises combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid. In one embodiment, the method comprises contacting the oxidant with a mixture comprising the phase transfer

catalyst (PTC), one or more metal oxides and the inorganic acid. In one embodiment, the method comprises contacting the oxidant with a mixture comprising the phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by addition of the inorganic acid.

5 In one embodiment, the combination of phase transfer catalyst (PTC), one or more metal oxides, oxidant and the inorganic acid, as described herein, forms a reaction mixture.

 In one embodiment, contacting the oxidant with the mixture comprising the PTC, one or more metal oxides and inorganic acid forms the reaction mixture.

10 In one embodiment, contacting the oxidant with the mixture comprising the PTC and one or more metal oxides; followed by addition of the inorganic acid forms the reaction mixture.

 In another aspect, the method of preparing the catalyst system disclosed herein comprises combining a PTC and oxidant followed by addition of a metal oxide and
15 inorganic acid.

 In one embodiment, combining the PTC and oxidant followed by addition of a metal oxide and inorganic acid forms the reaction mixture.

 The reaction mixture may comprise: non-reacted or partially reacted ingredients comprising the oxidant, PTC, one or more metal oxides, and inorganic acid; or an
20 oxidised catalyst mixture following reaction of the oxidant, PTC, one or more metal oxides and inorganic acid; or a combination of both.

 In one embodiment, the reaction mixture may comprise: non-reacted or partially reacted ingredients comprising the oxidant, PTC, one or more metal oxides, and inorganic acid; or an oxidised catalyst mixture following reaction of the oxidant with the
25 mixture of ingredients comprising PTC, one or more metal oxides and inorganic acid; or a combination of both.

 In one embodiment, reaction of the combination of phase transfer catalyst (PTC), one or more metal oxides, oxidant and inorganic acid as disclosed herein forms the oxidised catalyst mixture.

In one embodiment, reaction following the combination of the PTC and oxidant followed by addition of the one or more metal oxides and inorganic acid forms the oxidised catalyst mixture.

5 In one embodiment, reaction following contacting the oxidant with the mixture comprising PTC, one or more metal oxides and inorganic acid forms the oxidised catalyst mixture

In one embodiment, reaction following contacting the oxidant with the mixture comprising the PTC and one or more metal oxides; followed by addition of the inorganic acid forms an oxidised catalyst mixture.

10 In one embodiment, the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid and agitated for a period of time to form the oxidised catalyst mixture. In one embodiment, the oxidant is contacted with the mixture comprising PTC and one or more metal oxides; followed by addition of inorganic acid and agitated for a period of time to form the oxidised catalyst mixture.

15 In one embodiment, the oxidant is contacted with the PTC, followed by addition of one or more metal oxides and inorganic acid and agitated for a period of time to form the oxidised catalyst mixture.

Agitation may occur for at least about 1 sec to at least about 30 min including, at least about, 1s, 5s, 10s, 20s, 30s, 40s, 50s, 1 min, 5, min, 10 min, 15 min or 30 minutes.

20 Agitation may be achieved by stirring. Stirring may be achieved by an appropriate mixer as known by a person skilled in the art including but not limited to high shear mixers or pumps, in-line mixers, baffled vessels and the like.

The oxidised catalyst mixture comprises the catalyst system disclosed herein.

25 In some embodiments the reaction mixture comprises the oxidised catalyst mixture.

When the reaction mixture comprises the oxidised catalyst mixture it will be understood that the reaction mixture comprises the catalyst system disclosed herein. Accordingly, the phrases “oxidised catalyst mixture” and “reaction mixture comprising the oxidised catalyst mixture” will be understood to mean that the catalyst system of the
30 invention is comprised therein.

Accordingly, it will be understood that the catalyst system of the present disclosure is present in the oxidised catalyst mixture. It will also be understood that the catalyst system of the present disclosure is contained in the oxidised catalyst mixture which may or may not be present in the reaction mixture prior to agitation.

5 In some embodiments, contacting the oxidant with a mixture comprising the PTC, one or more metal oxides and inorganic acid forms a reaction mixture comprising oxidised catalyst mixture. In some embodiments, the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid and agitated for a period of time to form an oxidised catalyst mixture.

10 In some embodiments, contacting the oxidant with the PTC, followed by addition of one or more metal oxides and inorganic acid forms a reaction mixture comprising oxidised catalyst mixture.

 The catalyst system disclosed herein is present in the oxidised catalyst mixture and in the reaction mixture comprising the oxidised catalyst mixture. In one
15 embodiment, the catalyst system is separated from the reaction mixture comprising the oxidised catalyst mixture and optionally purified. In one embodiment the catalyst system is separated from the oxidised catalyst mixture and optionally purified.

 The catalyst system disclosed herein may be used with or without separation or purification from the reaction mixture comprising the oxidised catalyst mixture as herein
20 before described. In one embodiment, the catalyst system is not further isolated and/or separated from the oxidised catalyst system.

 The catalyst system disclosed herein may be used with or without separation or purification from the oxidised catalyst mixture as herein before described.

 The catalyst system disclosed herein is effective as a catalyst with hydrogen
25 peroxide in a process of reducing sulphur levels in a hydrocarbon stream containing sulphur, when present in the reaction mixture comprising the oxidised catalyst mixture or in the oxidised catalyst mixture optionally in separated or purified form.

 In some embodiments, the catalyst system is present in the reaction mixture comprising the oxidised catalyst mixture as herein before described. In one embodiment
30 the reaction mixture comprising the oxidised catalyst mixture further comprises one or more nonreacted or partially reacted ingredients including PTC, one or more metal oxide,

inorganic acid and/or oxidant. Such a reaction mixture comprising the catalyst system, may be referred to as a “one pot” catalyst mixture. As used herein “one pot” refers to making and using the catalyst system without separation and/or isolation from the reaction mixture in which it was formed. In some embodiments, the reaction mixture
5 comprising the catalyst system disclosed herein is used as a one pot catalyst mixture in a process for desulphurising a hydrocarbon stream containing sulphur.

In some embodiments, the catalyst system has a pH value of less than 7.

Multiple layers formed when preparing catalyst system

10 The reaction mixture comprising the oxidised catalyst mixture may comprise multiple layers. In some embodiments, the multiple layers form following stirring and/or settling of the reaction mixture comprising the oxidised catalyst mixture. The multiple layers may comprise one or more water immiscible layers. The multiple layers may comprise one or more water immiscible layers and an aqueous layer. In one embodiment,
15 the reaction mixture comprising the oxidised catalyst mixture comprises one or more water immiscible layers. In one embodiment, the reaction mixture comprises one or more water immiscible layers and an aqueous layer.

The oxidised catalyst mixture may comprise multiple layers. In one embodiment two layers are formed. In one embodiment three layers are formed. In some
20 embodiments, the multiple layers form following stirring and/or settling of the oxidised catalyst mixture. The multiple layers may comprise one or more water immiscible layers. The multiple layers may comprise one or more water immiscible layers and an aqueous layer. In one embodiment, the oxidised catalyst mixture comprises one or more water immiscible layers. In one embodiment, the oxidised catalyst mixture comprises one or
25 more water immiscible layers and an aqueous layer. In one embodiment, a water immiscible layer and an aqueous layer form. In one embodiment, two water immiscible layer and an aqueous layer form.

As used herein, “water immiscible layer” refers to a layer that forms a separate layer to an aqueous layer. A separate water immiscible layer to the aqueous layer may
30 form for a number of reasons including but not limited to the predominant presence of: an immiscible solvent and/or a substance that does not dissolve in aqueous solution. As

used herein, “substance” may include any starting ingredient, feedstock component, intermediate or final product from the process of making the catalyst system described herein or the process of desulphurising a hydrocarbon stream containing sulphur using a recycled catalyst system as disclosed herein. By “predominant presence” it will be understood that the solvent and/or substance referred to is in a quantity sufficient to impart the stated quality. By way of example, a substance that does not dissolve in aqueous solution that is predominantly present is a hydrocarbon. The water immiscible layer may be more or less dense than the aqueous layer which will result in the layer sitting below or above the aqueous layer.

10 In the case of a recycled catalyst system, the water immiscible layer may comprise the catalyst system, hydrocarbons, water and sulphones. The presence of sulphone in the water immiscible layer occurs post oxidation following oxidation of the sulphur in the hydrocarbon material and subsequent absorption of the oxidised sulphur compounds by the catalyst system. As discussed later, this absorption of oxidised sulphur compound
15 (e.g. sulphone) results in an increase in mass of the catalyst system with each subsequent oxidation as it absorbs oxidised sulphur compound (e.g. sulphone).

In some embodiments, the water immiscible layer comprises the oxidised catalyst mixture. In one embodiment, the water immiscible layer comprises the catalyst system. In one embodiment, the water immiscible layer is present as two separate water
20 immiscible layers. The two separate water immiscible layers may be a water immiscible layer comprising the catalyst system and a water immiscible layer comprising an organic material such as hydrocarbons.

It will be understood that the water immiscible layer may contain a small amount of the aqueous layer, either by molecular hydration or by occlusion/emulsion. Similarly,
25 it will be appreciated that the aqueous layer may contain a small amount of water immiscible layer. In one embodiment, the water immiscible layer is predominantly water immiscible, such that the layer may comprise a small amount of aqueous layer but not enough to impart aqueous characteristics as would be understood by a person skilled in the art. In one embodiment, the aqueous layer is predominantly aqueous, such that the
30 layer may comprise a small amount of water immiscible layer but not enough to impart water immiscible characteristics as would be understood by a person skilled in the art.

In some embodiments, more than one water immiscible layer is present. In one embodiment, two water immiscible layers are present. In one embodiment one water immiscible layer comprises the catalyst system disclosed herein and another water immiscible layer is an organic layer comprising an organic solvent. Multiple water
5 immiscible layers may form if, for instance, the PTC contains hydrocarbons.

Without being bound by theory, the inventors have presented 2 scenarios where two and three layers may be formed from an oxidised catalyst mixture or a reaction mixture comprising the same.

10 Two and three layers formed when preparing catalyst system

In one embodiment, the method of preparing the catalyst system disclosed herein comprises forming a reaction mixture comprising an oxidised catalyst mixture which comprises one or more layers.

In one embodiment, the method of preparing the catalyst system disclosed herein
15 comprises combining a phase transfer catalyst (PTC) and one or more metal oxides, followed by addition of an oxidant and an inorganic acid, to form a reaction mixture comprising an oxidised catalyst mixture which comprises one or more layers.

In one embodiment, the method of preparing the catalyst system disclosed herein
20 comprises contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC), one or more metal oxides and an inorganic acid to form a reaction mixture comprising an oxidised catalyst mixture which comprises one or more layers.

In one embodiment, the method comprises contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by addition of an inorganic acid.

25 In one embodiment, the method of preparing the catalyst system disclosed herein comprises contacting the oxidant with a PTC, followed by addition of one or more metal oxides and inorganic acid, to form a reaction mixture comprising oxidised catalyst mixture which comprises one or more layers.

The number and type of layers formed will depend on a number of factors
30 including but not limited to: the nature of the starting materials used to form the catalyst system, including the number of carbon atoms contained in the PTC, the presence of

water, the pH, the solubility of the ingredients in water, the nature of the metal and the presence of any other atoms, ions or molecules; and whether the reaction mixture comprising the oxidised catalyst mixture has been combined with a catalyst system recycled from a desulphurisation process as disclosed herein, where it has been in contact with a hydrocarbon stream. In one embodiment two layers are formed. In another embodiment three layers are formed. In another embodiment two water immiscible layers and an aqueous layer are formed. One water immiscible layer may comprise the catalyst system disclosed herein and another immiscible layer may comprise a layer that is predominantly hydrocarbons.

Two layers

In one embodiment, the PTC and metal oxide dissolve in water and the acid and oxidant are aqueous solutions. Accordingly, in this embodiment, water is present when the oxidised catalyst mixture is formed. Without being bound by theory, the inventors believe the catalyst system formed will have predominantly water immiscibility properties if it has predominantly organic character, such as a high carbon content, which means that it forms a separate layer to the aqueous layer.

In one embodiment, the catalyst is prepared using a PTC that is a quaternary ammonium salt (such as DDAHS or about a 80:20 mixture of DDAHS and DDAC) that dissolves in water, sodium tungstate that dissolves in water, aqueous phosphoric acid and aqueous hydrogen peroxide. Without being bound by theory, it is contemplated that as the quaternary ammonium cation in the ion pair with the phosphotungstate or oxophosphotungstate in the catalyst system has a high carbon atom count, with 22 carbons in the case of DDA, this likely contributes to its organic character that means it does not dissolve in water.

Three layers

In one embodiment, the PTC is dissolved or suspended in an organic solvent, such as hydrocarbons, the metal oxide dissolves in water and the acid and oxidant are aqueous solutions. The presence of an organic solvent in the reaction mixture may, amongst other reasons, result from the PTC requiring an organic solvent to dissolve or be suspended, or

as result of combining the reaction mixture comprising the catalyst system with a catalyst system recycled from desulphurisation process as disclosed herein, where it has been in contact with a hydrocarbon stream. Accordingly, in this embodiment, water and an organic solvent are present in the reaction mixture comprising the oxidised catalyst mixture.

Without being bound by theory, the inventors believe the catalyst system formed has predominantly water immiscibility properties which means that it forms a separate layer to the aqueous layer.

In one embodiment, the reaction mixture comprising the oxidised catalyst mixture forms three layers wherein one layer comprises an aqueous layer comprising one or more of excess oxidant, metal oxide and/or acid that was not incorporated in the formation of the catalyst system.

In one embodiment, the reaction mixture comprising the oxidised catalyst mixture forms three layers wherein one layer comprises a water immiscible layer which is an organic layer comprising organic solvent introduced with the PTC and/or hydrocarbon solvent from the recycled catalyst system.

In one embodiment, the reaction mixture comprising the oxidised catalyst mixture forms three layers comprising a water immiscible layer comprising the oxidised catalyst mixture comprising the catalyst system disclosed herein.

In some embodiments, the catalyst system is separated and/or isolated and optionally purified from the reaction mixture. Isolation of the catalyst system may be performed by a physical separation of layers using known methodology. In one embodiment, the water immiscible layer containing the catalyst system is separated from the aqueous layer and any other water immiscible layer. It will be appreciated that when the process of preparing the catalyst system is carried out on a small scale, the separation of the catalyst layer may be more difficult than when carried out on a larger scale preparation. Whilst purification of the catalyst is not required to benefit from the activity of the catalyst system disclosed herein, it is envisaged that purification may be achieved by treatment with solvents such as hydrocarbons, water or other solvents or by conventional methods known to one skilled in the art.

In some embodiments, the water immiscible layer comprising the oxidised catalyst mixture is separated from the reaction mixture. The separated water immiscible layer comprising the oxidised catalyst mixture may be used in a process for desulphurising a hydrocarbon material containing sulphur.

5 In one embodiment, the catalyst is prepared using a PTC that is a quaternary ammonium salt (such as a mixture of methyl tricaprylammonium hydrogen sulphate and methyl tricaprylammonium chloride) that is dissolved or suspended in hydrocarbon (diesel), sodium tungstate that dissolves in water, aqueous phosphoric acid and aqueous hydrogen peroxide. In this situation 3 layers are formed:

10 Layer 1: aqueous layer that contains any excess hydrogen peroxide and any tungstate and phosphoric acid that did not get incorporated in the water immiscible layer comprising the catalyst system.

Layer 2: the hydrocarbon solvent introduced with the PTC or hydrocarbon that was carried over during the recycle of the catalyst system from the previous
15 desulphurisation oxidation step.

Layer 3: This is the small-volume layer that comprises the catalyst system which may be in the form of a suspension, plus hydrocarbon solvent and water.

In one embodiment the method of preparing a catalyst system, comprises the steps of a) combining sodium tungstate dihydrate and an aqueous quaternary ammonium salt
20 to form a metal oxide and quaternary ammonium salt mixture; b) adding aqueous phosphoric acid to the metal oxide and quaternary ammonium salt mixture to form a reaction mixture; followed by c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst mixture; d) allowing the oxidised catalyst mixture to settle to form multiple layers including a water-immiscible layer containing the catalyst system; and d)
25 optionally separating the water immiscible layer containing the catalyst system.

In one embodiment, step a) involves combining the sodium tungstate dihydrate and aqueous quaternary ammonium salt (PTC) to allow dissolution or suspension of the sodium tungstate dihydrate in the PTC.

In another embodiment, the method of preparing a catalyst system comprises the
30 steps of a) combining sodium tungstate dihydrate and aqueous didecyl dimethylammonium hydrogen sulphate (DDAHS) to allow dissolution of the sodium

tungstate dihydrate in DDAHS to form a dissolved metal solution; b) adding aqueous phosphoric acid to the dissolved metal solution; followed by c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst solution; d) allowing the oxidised catalyst solution to settle to form 2 layers including a water-immiscible layer containing the catalyst system; and e) optionally separating the water immiscible layer containing the oxidised catalyst solution.

In one embodiment, in step a) sodium tungstate dihydrate is combined with an aqueous solution of didecyl dimethylammonium hydrogen sulphate and didecyl dimethylammonium hydrogen chloride with a ratio of the anions hydrogen sulphate :chloride of 80:20 (DDAHS/DDAC) or higher than 80 HS:20 Cl, to allow dissolution of the sodium tungstate dihydrate in DDAHS/DDAC to form a dissolved metal solution.

In another embodiment, the method of preparing a catalyst system comprises the steps of a) combining sodium tungstate dihydrate and a mixture of methyl tricaprylyl ammonium hydrogen sulphate and methyl tricaprylyl ammonium chloride dissolved or suspended in hydrocarbon (e.g. diesel) to form a reaction mixture; b) adding aqueous phosphoric acid to the reaction mixture; followed by c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst solution; d) allowing the oxidised catalyst solution to settle to form multiple layers, such as 3 layers, including a water-immiscible layer containing the catalyst system; and e) optionally separating the water immiscible layer containing the oxidised catalyst solution.

Steps a) - d) may be carried out at ambient temperature. In step c), the aqueous hydrogen peroxide may be added and mixed for at least about 30 sec, 1 minute, 5 min, 10 min, 30 minutes and 60 minutes. In step d), the oxidised catalyst solution is allowed to settle for a period until multiple layers form including from about 10 sec to 30 sec to 10 minutes to one week or more.

Catalyst system stored for further use

In one embodiment the catalyst system is stored for future use. In one embodiment, the reaction mixture comprising the oxidised catalyst mixture is stored for future use. In one embodiment, the water immiscible layer comprising the oxidised catalyst mixture is stored for future use.

The inventors have found that both the reaction mixture comprising the catalyst system and the water immiscible layer comprising the catalyst system are stable upon storage. Both the reaction mixture and the water immiscible layer containing the catalyst system may be stored for about 3 months to about 3 years under ambient conditions. In one embodiment it is stored for up to about 3 years, or 2, years or 1 year or 6 months or 3 months for future use.

Catalysts system prepared and used *in situ*

The catalyst system may be formed *in situ*. In one embodiment, the reaction mixture comprising the oxidised catalyst mixture is prepared and used *in situ*. In one embodiment the reaction mixture comprising the oxidised catalyst mixture is prepared and used *in situ* in a process for desulphurising a hydrocarbon stream containing sulphur. In one embodiment, the catalyst system is not further separated or isolated from the oxidised catalyst mixture.

Method of preparing the Catalyst System

The present disclosure provides an economical and safe method of preparing a catalyst system which is highly reactive and effective in the oxidative desulphurisation of a hydrocarbon stream containing sulphur compounds.

The method of preparing the catalyst system disclosed herein comprises combining one or more phase transfer catalysts (PTC), one or more metal oxide oxides; one or more oxidants and one or more inorganic acids, wherein the method does not comprise combining the oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.

In one aspect, there is provided a method of preparing a catalyst system, the method comprising combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid.

In another aspect, there is provided a method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC); one or more metal oxide oxides; and an inorganic acid.

In another aspect, there is provided a method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxide oxides; followed by addition of an inorganic acid.

5 In another aspect, there is provided a method of preparing the catalyst system disclosed herein comprising combining a PTC and oxidant followed by addition of a metal oxide and inorganic acid.

The inventors have surprisingly found that the order of addition of the components of the catalyst system is important in providing the reactive catalyst system disclosed
10 herein. Importantly, the preparation of the catalyst system disclosed herein enables the use of significantly reduced amounts of the metal and oxidant compared to prior art preparations while maintaining a high level of catalytic activity. This has cost production benefits as the quantity of expensive metal components, such as the Group VIb metals tungsten and molybdenum, is much lower compared to the prior art as well as reducing
15 the amount of expensive oxidant. For instance, in one embodiment, up to a 99% reduction in the quantity of the Group VIb metal is achieved with comparable and better effectivity. The eventual discarding of any residual metal and oxidant will be significantly less which is advantageous from an environmental perspective. Additionally, the preparation of the catalyst system disclosed herein provides a safe methodology for producing a catalyst
20 system that is very useful in oxidative desulphurisation processes.

In one embodiment, the catalyst system prepared by the unique method disclosed herein is a liquid.

In one embodiment, there is disclosed a method of preparing a catalyst system comprising contacting the oxidant with a mixture comprising the PTC, one or more metal
25 oxides and the inorganic acid. In one embodiment, the one or more metal oxides is combined with the PTC prior to combining with the inorganic acid and oxidant. In one embodiment, the one or more metal oxides is added to the PTC. In one embodiment, the PTC is added to the one or more metal oxides.

In another embodiment, the oxidant is contacted with the PTC followed by
30 addition of a metal oxide and inorganic acid.

In one embodiment, there is disclosed a method of preparing a catalyst system comprising: a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC; b) adding the inorganic acid to the mixture of metal oxide and PTC followed by: c) addition of the oxidant.

5 In one embodiment, there is disclosed a method of preparing a catalyst system as disclosed herein wherein the oxidant is contacted with the mixture of PTC, one or more metal oxides and inorganic acid and agitated for a period of time to form an oxidised catalyst mixture. In one embodiment, agitation occurs for at least about 1 sec, 2 sec, 5, sec, 10 sec, 15 sec 20, sec, 30, sec, 45 sec, 1 min, 2, min, 3, min, 4 min, 5min 10 min, 15
10 min or 30 minutes. In one embodiment, multiple layers form following settling of the oxidised catalyst mixture. In one embodiment, two or three layers are formed. In one embodiment, a water immiscible layer and an aqueous layer form as defined herein. In one embodiment, two water immiscible layers and an aqueous layer form as defined herein.

15

Metal oxide

One or more metal oxides is used in the preparation of the catalyst system disclosed herein. In one embodiment a Group VIb metal oxide is used. The Group VIb metal oxide may be in the form of a metal acid, metal trioxide, or a metal tetraoxide or
20 salt thereof optionally as a hydrate. The Group VIb metal oxide may be a mixture of two or more Group VIb metal oxides.

In one embodiment the Group VIb metal is tungsten and/or molybdenum. In one embodiment the Group VIb metal oxide is in acid form, such as tungstic acid and/or molybdic acid. In one embodiment the Group VIb metal oxide is a Group VIb metal trioxide, such as tungsten trioxide WO_3 and/or molybdenum trioxide. In one embodiment
25 the Group VIb metal oxide is in the form of a tetraoxide and/or its salt, such as a tungstate salt and/or molybdate salt. In one embodiment the Group VIb metal oxide is a tungstate salt and/or a molybdate salt. In one embodiment the Group VIb metal tetraoxide salt is a hydrate, including the monohydrate and/or dihydrate. In one embodiment the tungstate salt and/or a molybdate salt is a dihydrate. In one embodiment, the Group VIb metal
30 oxide is a salt wherein the cation may be a sodium or ammonium ion. In one embodiment,

the Group VIb metal oxide is a sodium tungstate dihydrate and/or a sodium molybdate dihydrate. In one embodiment the Group VIb metal oxide is sodium tungstate dihydrate.

In one embodiment the Group VIb metal oxide is selected from one or more of the following: tungstic acid, tungsten trioxide, tungstate salt (including sodium tungstate), tungstate salt dihydrate (including sodium tungstate dihydrate), molybdic acid, molybdic acid monohydrate, molybdic acid dihydrate, molybdenum trioxide, molybdate salt (including sodium molybdate), and molybdate salt dihydrate (including sodium molybdate dihydrate).

The metal oxide used in the preparation of the catalyst system may be in an amount of about 0.001 mole% of catalyst system to about 6 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system. In one embodiment, the metal oxide is in an amount of about 0.3 mole% of catalyst system.

In one embodiment a metal oxide is sodium tungstate dihydrate.

15 Inorganic acid

An inorganic acid is used in the preparation of the catalyst system disclosed herein. In one embodiment, the inorganic acid comprises a phosphorous containing inorganic acid.

The inorganic acid may be phosphoric acid or amino-phosphonic acid. Any commonly commercially available concentration of phosphoric acid or amino-phosphonic acid may be used. In one embodiment, the inorganic acid is aqueous phosphoric acid. In one embodiment, about 75 - 85% aqueous phosphoric acid is used. In one embodiment, about 81% aqueous phosphoric acid is used.

Without being bound by theory, the inventors believe the phosphoric acid provides a source of phosphorous in the catalyst system and serves to adjust the pH.

In one embodiment, the inorganic acid may be any acid, such as hydrochloric acid, sulphuric, acetic acid and other acids in combination with an inorganic source of phosphorous, such as sodium phosphate, potassium phosphate, sodium hydrogen phosphate, potassium hydrogen phosphate, sodium dihydrogen phosphate or potassium dihydrogen phosphate, where the resulting pH is less than 7.

In another embodiment, the inorganic acid comprises a non-phosphorous inorganic acid and a phosphorous containing inorganic acid.

In one embodiment, the inorganic acid is in an amount of about 0.001 mole% of catalyst system to about 6.0 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system. In one embodiment the inorganic acid is in an amount of about 0.3 mol% of catalyst system.

The inorganic acid may be aqueous phosphoric acid (such as 81 % aq).

10 Phase-Transfer Catalyst (PTC)

A phase-transfer catalyst (PTC) is used in the preparation of the catalyst system disclosed herein.

The phase-transfer catalyst (PTC) may be selected from catalysts known to a person skilled in the art including those described in "Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives" by Starks, Liotta and Halpern, 15 Chapman and Hall, 1994.

The PTC used in the method disclosed herein includes but is not limited to the group consisting of quaternary ammonium salts, quaternary phosphonium salts, guanidinium salts, such as hexaalkyl guanidinium salts, N-quaternized heterocyclic 20 compounds, such as pyridinium salts or imidazolium salts, phosphazanium salts and linear or cyclic polyethylene glycols and their ethers, including cyclic crown ethers and cryptands. In one embodiment, the phase-transfer catalyst is a quaternary ammonium salt that comprises a cation Q^+ and an anion X^- .

In one embodiment, the PTC comprises one or more quaternary ammonium salts.

25 Phase-transfer catalysts include a cation, or multiple cations, and an anion or multiple anions.

Quat Cation, Q^+

Suitable phase-transfer catalyst (PTC) cations include but are not limited to 30 quaternary ammonium cations, quaternary phosphonium cations, quaternary pyridinium cations and quaternary guanidinium cations.

In one embodiment, the PTC cations may be a tetraalkyl ammonium cation, tetraalkyl phosphonium cation, tetraaryl phosphonium cation and alkyl triaryl phosphonium cation.

Examples of suitable phase-transfer catalyst cations include but are not limited to
5 methyl tricaprylyl ammonium, methyl trioctyl ammonium, methyl tridecyl ammonium, methyl tributyl ammonium, tetrabutyl ammonium, tetrapropyl ammonium, tetraethyl ammonium, methyl tridodecyl ammonium, octyl tributyl ammonium, dimethyl didecyl ammonium, hexadecyl trimethyl ammonium, stearyl trimethyl ammonium, tetraoctyl ammonium, tetrahexyl ammonium, hexadecyl tributyl ammonium, tetraoctadecyl
10 ammonium, tetrabutyl phosphonium, trihexyl tetradecyl phosphonium, tetraoctyl phosphonium, cetyl pyridinium, hexaethyl guanidinium, hexabutyl guanidinium and other tetraalkyl ammonium and phosphonium cations, hexaalkyl guanidinium cations and alkyl pyridinium cations.

In one embodiment, the PTC cations are quaternary ammonium cations or
15 quaternary phosphonium cations which have a total number of carbon atoms of 18 or more. In one embodiment the total number of carbon atoms is in a range of about 18 to 72 carbon atoms.

In one embodiment, the cation Q^+ is a quaternary ammonium cation that comprises a central nitrogen atom bound to four alkyl groups.

20 In one embodiment, quaternary ammonium cation that comprises a central nitrogen atom bound to four alkyl groups that have a total of at least 18 carbon atoms.

In one embodiment, the alkyl groups have a total in the range of 22 to 48 carbons atoms.

In one embodiment, the PTC is a tetraalkylammonium cation. In one embodiment
25 the alkyl groups of the tetraalkyl ammonium cation are independently C1-18 alkyl groups. In one embodiment, the alkyl groups have a total of at least 18 carbon atoms, at least 22 carbon atoms, or in the range of 18 - 48 or 22 - 48 carbons atoms. In one embodiment the alkyl groups are independently C1-12 alkyl groups. In one embodiment the alkyl groups are independently C1-10 alkyl groups. In one embodiment the cation is
30 a methyl triC8-C10alkyl ammonium cation. In one embodiment the cation is a dimethyl diC10alkyl ammonium cation.

In one embodiment, the PTC cation is methyl tricaprylyl ammonium, methyl trioctyl ammonium, methyl tridecyl ammonium, methyl tridodecyl ammonium, octyl tributyl ammonium, dimethyl didecyl ammonium, hexadecyl trimethyl ammonium, stearyl trimethyl ammonium, tetraoctyl ammonium, tetrahexyl ammonium, hexadecyl tributyl ammonium, tetraoctadecyl ammonium, trihexyl tetradecyl phosphonium, tetraoctyl phosphonium, cetyl pyridinium, hexaethyl guanidinium, hexabutyl guanidinium and other tetraalkyl ammonium and phosphonium cations, hexaalkyl guanidinium cations and alkyl pyridinium cations.

In one embodiment, the PTC cation is methyltrioctyl ammonium. In one embodiment, the PTC cation is tetraoctyl ammonium. In one embodiment, the PTC cation is methyl tridecyl ammonium. In one embodiment the PTC cation is dimethyl didecyl ammonium. In one embodiment, the PTC cation is a mixture of methyltrioctyl ammonium and methyl tridecyl ammonium.

15 Anion, X^-

The anion X^- may be any anion.

The anion in an ion pair $\{Q^+X^-\}$ between a quaternary ammonium cation, Q^+ , and an anion, X^- , can be exchanged for another anion, Y^- , by mixing the salt of Y^- , such as Na^+Y^- or K^+Y^- (M^+Y^-) with Q^+X^- . The extent to which Q^+X^- will be converted to Q^+Y^- when mixed with M^+Y^- is governed by thermodynamic factors.

The ion exchange of Q^+X^- with M^+Y^- to form Q^+Y^- and M^+X^- can be very easily performed in many cases by simply mixing Q^+X^- and M^+Y^- in systems known to a person skilled in the art.

Suitable phase transfer catalyst (PTC) **anions** include but are not limited to phosphotungstate, oxophosphosphotungstate, phosphomolybdate, oxophosphomolybdate, halide, hydrogen sulphate, methyl sulphate, sulphate, phosphate, carbonate, hydrogen carbonate, methanesulphonate or a combination thereof.

In one embodiment, the anion X^- is selected from the group consisting of phosphotungstate, phosphomolybdate, oxophosphosphotungstate, oxophosphomolybdate, hydrogen sulphate, methyl sulphate, chloride and bromide.

Without being bound to theory, when the anion X^- is not phosphotungstate, phosphomolybdate, oxophosphotungstate, oxophosphomolybdate, then it is preferable for the anion X^- , to have a lower affinity for the quaternary ammonium cation Q^+ rather than a higher affinity, as described in de la Zerda, J.; Sasson, Y.; J. Chem. Soc. Perkin Trans. II, 1987, 1147 and in "Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives" by Starks, Liotta and Halpern, Chapman and Hall, 1994, page 27.

Without being bound to theory, the anions with a lower affinity for pairing with the quaternary ammonium cation Q^+ enable a higher extent of ion exchange of the anion X^- for phosphotungstate, phosphomolybdate, oxophosphotungstate or oxophosphomolybdate which are examples of anions used in the preparation of the oxidation catalyst system disclosed herein. For example, chloride has a lower affinity for quaternary ammonium cations Q^+ than bromide. Therefore, Q^+Cl^- is preferable over Q^+Br^- as the quaternary ammonium salt component of the phase-transfer catalyst, since when mixing Q^+Cl^- with sodium phosphotungstate, phosphomolybdate, oxophosphotungstate or oxophosphomolybdate, more of the quaternary ammonium cation Q^+ will pair with phosphotungstate, phosphomolybdate, oxophosphotungstate or oxophosphomolybdate compared to mixing Q^+Br^- with sodium phosphotungstate, phosphomolybdate, oxophosphotungstate or oxophosphomolybdate.

In one embodiment, the anion X^- is selected from the group consisting of halides (such as chloride and bromide), hydrogen sulphate, methyl sulphate, sulphate and phosphate or combinations thereof.

In one embodiment, the anions X^- include chloride, bromide, hydrogen sulphate and methyl sulphate.

In one embodiment the anion is a chloride, hydrogen sulphate or a mixture of chloride and hydrogen sulphate.

Interactions and Choices of Quaternary Cation, Q^+ , Anion X^- and Group VIb metal Oxide

The below is a consideration of one embodiment of the catalyst system disclosed herein when the PTC is a quaternary ammonium salt, Q^+X^- .

Without being bound by theory, the role of the quaternary ammonium cation Q^+ is to impart significant organophilicity to the ion pair Q^+X^- so that it will be compatible from a polarity standpoint with the nonpolar components of the hydrocarbon fuel feedstock including the hydrocarbon compounds and the organic sulphides. This may be important, for instance, when the alkali Group VIb metal salts of phosphotungstate, phosphomolybdate, oxophosphotungstate and oxophosphomolybdate anions, being examples of the anions used in the preparation of the catalysts system disclosed herein, are inorganic salts and, as such, have very low affinity for the nonpolar organic hydrocarbon compounds and their organic sulphides. The inventors have observed that the oxidation of the organic sulphides does not take place in the absence of a phase-transfer catalyst, even when the sodium salts of phosphotungstate, oxophosphotungstate, phosphomolybdate or oxophosphomolybdate are present.

The inventors have also observed that when the quaternary ammonium cation, Q^+ has a total of 16 carbon atoms or less, such as tetrabutylammonium (16 carbon atoms total) or tetramethyl ammonium (4 carbon atoms total), the catalytic activity for desulphurisation is reduced dramatically compared to the catalytic activity for desulphurisation when the quaternary ammonium cation, Q^+ has a total of 18 carbon atoms or more such as hexadecyl trimethyl ammonium (19 carbon atoms total), didecyl dimethyl ammonium (22 carbon atoms total), methyl trioctyl ammonium (25 carbon atoms total), tetraoctyl ammonium (32 carbon atoms total) or methyl tridodecyl ammonium (37 carbon atoms total).

A necessary but insufficient component of the oxidation catalyst system disclosed herein is the Group VIb metal oxide, for example a Group VIb metal oxide which includes anions such as a phosphotungstate, phosphomolybdate, oxophosphotungstate or oxophosphomolybdate that will be referred to as " Ox^- ". As described above and without being bound to theory, since the Ox^- anion is ineffective as an oxidation catalyst in the absence of an organophilic quaternary ammonium cation, Q^+ , then it is believed that the active form of the oxidation catalyst system disclosed herein is an ion pair, Q^+Ox^- .

PTC (Q^+X^-)

In one embodiment, the PTC (represented by Q^+X^-) used in the preparation of the catalyst system disclosed herein is selected from the quaternary cations Q^+ and the anions X^- as hereinbefore described.

- 5 In one embodiment, the PTC is selected from quaternary ammonium salts wherein the cation has a total number of carbons of at least 18 carbons. In one embodiment, the PTC is selected from the group consisting of: tetraalkyl ammonium hydrogen sulphates and tetraalkyl ammonium halides (such as chloride and bromide), wherein the total number carbons in the tetraalkyl component is at least 18 carbons, and mixtures thereof.
- 10 In one embodiment, the tetraalkyl ammonium hydrogen sulphates include but are not limited to methyltricaprylammonium hydrogen sulphate and didecyl dimethylammonium hydrogen sulphate (DDAHS). In one embodiment, the tetraalkyl ammonium halides include but are not limited to didecyl dimethylammonium chloride (DDAC), methyltricaprylammonium chloride, didecyl dimethylammonium chloride (DDAC), methyltricaprylammonium chloride, tetraoctylammonium chloride and
- 15 tetraoctylammonium bromide.

In some embodiments, the quaternary ammonium salt dissolves in aqueous solution.

- In one embodiment, the PTC is didecyl dimethylammonium hydrogen sulphate (DDAHS). In one embodiment the DDAHS dissolves in an aqueous solution and is in the form of aqueous DDAHS.
- 20

In one embodiment, the didecyl dimethylammonium hydrogen sulphate (DDAHS) is prepared from didecyl dimethylammonium chloride (DDAC). Replacing the Cl^- with HSO_4^- may be achieved according to known techniques.

- 25 In one embodiment, the PTC is a mixture of aqueous DDAC and DDAHS. This scenario may arise from the conversion of DDAC to DDAHS where there may not be a quantitative removal of all the Cl^- anions, resulting in a quaternary ammonium salt with more than a single anion, i.e chloride and hydrogen sulphate anions.

- A DDAHS/DDAC mixture may be formed from DDAC. In one embodiment, the aqueous sulphuric acid is added to DDAC, followed by addition of sodium tungstate, then phosphoric acid, followed by hydrogen peroxide. In one embodiment, the
- 30

DDAHS/DDAC mixture has a ratio of the anions hydrogen sulphate:chloride of 80:20 (DDAHS/DDAC) or higher than 80 HS:20 Cl. In one embodiment, the DDAHS/DDAC mixture has a ratio of about 98:2 (DDAHS/DDAC).

The above embodiments are applicable when didecyl dimethylammonium bromide is used in place of didecyl dimethylammonium chloride.

In one embodiment, the PTC is selected from quaternary ammonium hydrogen sulphates and quaternary ammonium chlorides and mixtures thereof.

In one embodiment, the PTC is selected from didecyl dimethylammonium hydrogen sulphate (DDAHS) and didecyl dimethylammonium chloride (DDAC) and mixtures thereof. In one embodiment, the PTC is didecyl dimethylammonium with an anion ratio of about 80% hydrogen sulphate to 20% chloride.

In one embodiment, the PTC is selected from methyltricaprylammonium hydrogen sulphate and methyltricaprylammonium chloride and mixtures thereof. In one embodiment, the PTC is methyltricaprylammonium with an anion ratio of about 80% hydrogen sulphate to 20% chloride.

In one embodiment, the PTC used in the preparation of the catalyst system is in an amount of about 2.5 mole% of catalyst system to about 3.5 mole % of catalyst system; or about 3.0 mole% of catalyst system to about 3.3 mole % of catalyst system. In one embodiment, the PTC is present as about 3.2 mole % of catalyst system.

In one embodiment, the molar ratio of metal oxide to PTC (e.g. quaternary ammonium salt – “Quat”) is in a range of about 0.5:1 to 0.0004:1; or about 0.18:1 to 0.005:1. In one embodiment, the ratio metal oxide to PTC is about 0.09:1.

Whilst the molar ratio of PTC (e.g. quaternary ammonium salt – “Quat”) to tungsten (in the metal oxide) is relatively high, the molar ratio of the catalyst system to sulphur that is oxidised in the hydrocarbon material is very low as will be described below when compared to prior art methodology.

Oxidant

An oxidant is used in the preparation of the catalyst system disclosed herein. It will be understood by the skilled person that the oxidant may comprise one or more species which act as an oxidant.

In one embodiment the oxidant is an aqueous solution. The oxidant may be hydrogen peroxide or sodium hypochlorite. In one embodiment, the oxidant is aqueous hydrogen peroxide, including but not limited to about 20-70% aqueous hydrogen peroxide. In one embodiment, about 35% aqueous hydrogen peroxide is used. In another
 5 embodiment about 50% aqueous hydrogen peroxide is used.

In one embodiment, the oxidant used in the preparation of the catalyst is in a molar ratio of oxidant : metal oxide in the range of about 7000:1 to 100:1; or about 7000:1 to 300:1 or about 500:1.

The molar ratio of PTC : oxidant may be about 0.02:1 to 0.05:1; or about 0.03:1.
 10 Generally, the Quat (PTC) and H_2O_2 are used in nearly constant ratios, wherein $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and H_3PO_4 are variable and at surprisingly low molar ratios.

Molar ratio of PTC: metal oxide: inorganic acid: oxidant

In one embodiment the molar ratio of PTC : metal oxide : inorganic acid : oxidant
 15 is in a range of about 0.032: 0.0057: 0.0055: 0.96 to about 0.032: 0.00015: 0.00028: 0.97. In one embodiment the molar ratio of PTC: metal oxide: inorganic acid: oxidant is about 0.032: 0.0029: 0.0028: 0.96. The PTC may be DDAHS, DDAC or DDAHS. The metal oxide may be $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The inorganic acid may be phosphoric acid (H_3PO_4)(81%). The oxidant may be hydrogen peroxide (H_2O_2) (35%). In one embodiment, the molar
 20 ratio of DDAHS: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$: H_3PO_4 (81%): H_2O_2 (35%) is about 0.032024:0.002882:0.002788:0.962307.

Generally, the PTC (e.g. Quat) and oxidant (e.g. H_2O_2) are used in nearly constant ratios, wherein the metal oxide (e.g. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and inorganic acid (e.g. H_3PO_4) are variable and at surprisingly low molar ratios.

25

Advantages of Catalyst system

In one embodiment, the present disclosure provides a catalyst system that is economical and environmentally efficient when compared to prior art catalysts, such as, traditional hydrotreating catalysts which use battery metals such as Cobalt/Molybdenum
 30 (CoMo) or Nickel/Molybdenum (NiMo) catalyst. Specifically, the catalyst disclosed herein is efficient as it uses less Group VIb metal over the life of the hydrotreating bed

when compared to these traditional hydrotreating catalysts. In one embodiment, the use of the catalyst system disclosed herein in an oxidative desulphurisation (ODS) process, has many advantages over the hydrotreating desulphurization (HDS) that is being replaced by the present technology including but not limited to:

- 5 • significantly reduced carbon footprint when compared with HDS due to lower energy requirement as the operating conditions (pressure and temperature) are significantly lower than that of HDS.
 - ODS does not use hydrogen, has no gaseous waste and has significantly lower aqueous waste therefore avoiding the requirement for auxiliary systems to
10 treat gaseous waste and significant reduction in aqueous waste treatment.
 - Aqueous waste does not carry the toxicity of HDS aqueous waste so treatment is also simpler. ODS also has significantly lower capital cost than HDS due to milder operating conditions resulting to less expensive material of construction, overall simplicity of the process resulting to less equipment
15 required which translates to reduced manufacturing and installation time for an ODS unit to be manufactured, deployed and commissioned.
 - From a safety aspect, ODS is safer as it operates at low to mild operating temperatures and pressures compared to HDS and does not have highly volatile hydrogen present. Furthermore, unlike HDS which produces H₂S that
20 requires further treatment and particular metallurgy, ODS does not produce H₂S.
- The ODS system utilizes a very low Group VIb metal content liquid catalyst system. This avoid the potential for catalyst deactivation as the catalyst is being constantly renewed, and avoids the requirements of fixed bed catalyst
25 replacement and downtime. Fixed beds also produce toxic metals post bed life which require specialist treatment and disposal.

In one embodiment, the catalyst system is in liquid form and is continually being turned over which avoids the pitfalls associated with fixed bed catalyst. Also a single catalyst system as disclosed herein is used in the oxidative desulphurisation process
30 avoiding the configuration used in HDS, where a separate guard bed catalyst is employed to protect the active HDS catalyst.

Metals reduction over the life of the HDS fixed bed catalyst compared to use of the catalyst system disclosed herein over the same period results in a reduction of Group VIb metal between 75% and 50%.

As a liquid, the catalyst system has a very low loading of transition metals making
5 it cost effective for commercial operations.

Process of desulphurising a hydrocarbon stream containing sulphur

The catalyst system disclosed herein has been found to be extremely effective in the oxidative desulphurisation process.

10 The general process of oxidative desulphurisation is known to the inventors, an example of such a process is disclosed in WO2014/138810 and is incorporated by reference herein.

In one embodiment the present disclosure provides a process for reducing the sulphur content of a hydrocarbon stream containing sulphur compounds, the process
15 comprising: a) contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system prepared by the method disclosed herein, so as to oxidise at least a portion of the sulphur compounds in the hydrocarbon material to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and b)
20 separating at least a portion of the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon mixture with a reduced sulphur content.

There are different ways of combining the hydrocarbon material, hydrogen peroxide and the catalyst system to allow oxidation of the hydrocarbon mixture to occur. The catalyst system may be added to the hydrocarbon material followed by addition of the hydrogen peroxide or the catalyst system and hydrogen peroxide may be added
25 simultaneously to the hydrocarbon material.

The catalyst system may also be added to a mixture of the hydrocarbon material and the hydrogen peroxide with caution. It will be appreciated by the person skilled in the art that this order of addition is potentially hazardous and should be embarked on with caution.

30 The hydrocarbon material, hydrogen peroxide and the catalyst system may be mixed together as described above with agitation. Agitation may be achieved using

known mixing methodology such as reactor columns with internal mechanical force, such as a low shear paddle mixer to assist the mixing.

The oxidation reaction may take place in a reaction vessel that is static, stirred or agitated with for example, oscillating or rotating discs or paddles. The oxidation reaction may be carried out at a temperature of about 50-150°C, 50-100°C, 50-80°C or >50 °C, or >60 °C, or >70 °C, or >80 °C. The hydrocarbon material may be heated to, for example, greater than about 60°C. It may be heated before or after it comes in contact with the oxidant and catalyst system. The hydrocarbon material containing the sulphur compounds may be preheated before it is combined with the oxidant and catalyst system.

10 In one embodiment the hydrocarbon material is preheated to > 60 °C.

In one embodiment the oxidised catalyst mixture and the water immiscible layer as described herein comprise the catalyst system.

In one embodiment, the catalyst system used in the process is contained in the oxidised catalyst mixture.

15 In one embodiment, the catalyst system used in the process is contained in the water-immiscible layer. The catalyst system may or may not be isolated from the water immiscible layer.

In one embodiment the catalyst system is prepared and stored separately prior to use.

20 In one embodiment the catalyst system is prepared *in situ*.

Molar Ratio of hydrogen peroxide : sulphur in hydrocarbon stream

The catalyst system disclosed herein is used as a catalyst for the oxidative desulphurizing process disclosed herein.

25 The present inventors have surprisingly found that the catalyst system disclosed herein together with an oxidant, allows for a very efficient and economical use of the catalyst and oxidant in the oxidation and desulphurisation process of hydrocarbon material containing sulphur.

In one embodiment, the oxidant is used in stoichiometric quantities. Specifically,
30 the desulphurisation is enabled by the stoichiometric oxidation of the sulphur by the oxidant then separation of the resulting sulphones.

Whilst a broad range of molar ratio of hydrogen peroxide to sulphur in hydrocarbon stream containing sulphur ($\text{H}_2\text{O}_2:\text{S}$) may be used, such as the range of about 2:1 to about 9:1, the inventors have found that a smaller range of about 2:1 to about 5:1 and a range of about 2:1 to about 2.5:1 may be employed to effectively oxidise the sulphur to sulphone. The ability to be able to desulphurise at such a low level of only 2.0 - 5 and lower at 2.0 - 2.5 molar equivalents of oxygen to sulphur provides a significant economic advantage over known processes that use 10-20 times this amount or more in some reports.

It will be understood that a minimum of 2.0 molar equivalents of hydrogen peroxide to sulphur is required to convert all the sulphur (e.g., in the form of a sulphide) in the hydrocarbon stream to sulfoxide and then to the sulphone. Therefore, the use of less excess oxidant, for example only 0-0.5 molar equivalents, provides for a greener technology as well as a very significant cost savings and reduced oxidant handling logistics relative to using excess oxidant of 9.5-19.5 molar equivalents.

In one embodiment, the molar ratio of hydrogen peroxide to sulphur in the hydrocarbon stream containing sulphur ($\text{H}_2\text{O}_2:\text{S}$) is in a range of about 2:1 to about 2.5:1.

In one embodiment the molar ratio of hydrogen peroxide to sulphur in hydrocarbon stream containing sulphur ($\text{H}_2\text{O}_2:\text{S}$) is about 2.5:1.

In one embodiment, the mass ratio of catalyst system disclosed herein to sulphur in hydrocarbon stream containing sulphur (catalyst : S) is about 0.2:1. In one embodiment the mass ratio of catalyst : S is about 0.1 kg/kg to about 2.0 kg/kg; or about 0.1 kg/kg to about 0.5 kg/kg or about 0.2 kg/kg.

In one embodiment, the present disclosure uses a maximum of 2.5 moles of hydrogen peroxide per mole of sulphur in the hydrocarbon stream containing sulphur making the reaction a very efficient reaction. The cost of oxidant is a significant financial barrier as well as making a substantial contribution to the overall energy balance and carbon intensity depending in the production method used for the generation of hydrogen peroxide.

As demonstrated in the Examples, the present inventors have shown that oxidative desulphurisation of diesel using the catalysts system disclosed herein is highly efficient

compared to known methodology with regard to the amount of PTC, metal oxide and phosphoric acid used and its oxidative performance.

Extraction and other methods

5 In one embodiment, the target sulphur content of the hydrocarbon stream can be achieved using the above disclosed process with a single extraction mechanism, such as solvent extraction, which also has a positive contribution to overall energy efficiency. In contrast, prior art methodologies require fixed bed adsorption, either stand alone or in conjunction with solvent extraction, to achieve the desired sulphur result.

10 In the oxidative desulphurisation process disclosed herein, the oxidised sulphur compounds are separated from the oxidised hydrocarbon mixture to provide a hydrocarbon stream with reduced sulphur content.

 In one embodiment, at least a portion of the oxidised sulphur compounds are separated from the oxidised hydrocarbon mixture by solvent extraction. This provides a
15 hydrocarbon material with reduced sulphur content and an extractant comprising the oxidised sulphur compounds. The hydrocarbon material with reduced sulphur content may undergo further extraction with an extractant to allow further oxidised sulphur to be extracted until the desired level of sulphur in the hydrocarbon material is achieved.

 The extraction of the oxidised sulphur compounds may be carried out according
20 to known separation techniques. In one embodiment, the extraction may be carried out using solvent extraction. In one embodiment solvent extraction is carried out with a polar solvent selected from the group consisting of N-methyl pyrrolidone (NMP), acetonitrile, DMF (dimethyl formamide), DMSO (dimethyl sulphoxide), methanol, water, brine, furfural and an ionic solution or mixtures thereof. In one embodiment the extractant is a
25 mixture of N-methyl pyrrolidone (NMP) and water (aqueous NMP). This may be the a mixture of up to about 95% by weight NMP and 5% by weight water (5% aqueous NMP), or up to about 98% by weight N-methyl pyrrolidone and (2% by weight water (2% aqueous NMP). The weight ratio of NMP : oxidised hydrocarbon mixture may be in a range of about 0.2:1 to about 2:1, or about 0.4:1 to about 1:1. In one embodiment, the
30 ratio of NMP : oxidised hydrocarbon mixture is about 0.5:1.

The hydrocarbon stream with reduced sulphur content maybe contacted with an extractant to allow further oxidised sulphur to be extracted into the extractant. In one embodiment the extractant is an aqueous solution such as water or brine.

In one embodiment, at least a portion of the oxidised sulphur compounds may be separated from the oxidised hydrocarbon mixture using distillation such as batch distillation.

Sulphur content

The hydrocarbon material containing sulphur compounds that is to be subject to the oxidative desulphurisation process disclosed herein, may be feedstock hydrocarbon material containing sulphur in a range of about 10 ppm to 20000 ppm. In one embodiment the feedstock diesel fuel contains sulphur in the range of about 10-15000 ppm, or about 10-12000 ppm or about 10-10000 ppm, or about 10-5000 ppm, or about 10-1000 ppm, or about 10-500 ppm or about 10-100 ppm, or 100-15000 ppm, or about 100-12000 ppm or about 100-5000 ppm, or about 100-2000 ppm, or about 100-1000 ppm, or about 100-500 ppm or greater than about 200 ppm, 300 ppm, 500 ppm, 1000 ppm, or 5000 ppm or less than about 15,000 ppm. 12,000 ppm, 5000 ppm, 1000 ppm or 500 ppm, or about 280 ppm, or about 500 ppm, or about 12000 ppm, or about 15000 ppm relative to the mass of the feedstock diesel fuel.

In one embodiment the hydrocarbon stream containing sulphur compounds has a sulphur mass of greater than about 1000 ppm (0.1wt %) relative to the mass of the hydrocarbon stream containing sulphur.

In one embodiment the hydrocarbon stream containing sulphur compounds has a sulphur mass of less than about 1000 ppm relative to the mass of the hydrocarbon stream containing sulphur.

In one embodiment the hydrocarbon stream containing sulphur compounds is diesel.

In one embodiment the hydrocarbon stream containing sulphur compounds has a sulphur mass of greater than about 1000 ppm (0.1 wt%) relative to the mass of the hydrocarbon stream. Examples of hydrocarbon material containing sulphur compounds include but are not limited to diesel, clarified oil (including slurry oil) and heavy fuel oil (HFO), light cycle oil, recycled base oil, natural gas liquids (natural gas condensate).

In one embodiment, the hydrocarbon material is diesel fuel with a sulphur content of up to about 500 ppm.

In one embodiment, the oxidative desulphurisation process disclosed herein provides a diesel fuel with a sulphur level of <15 ppm or < 10ppm.

5 In one embodiment hydrocarbon material is gasoil with a sulphur content of up to about 13000 ppm.

In one embodiment, the oxidative desulphurisation process disclosed herein provides a gasoil with a sulphur level of approx. 5000ppm or < 5000 pm.

10 In one embodiment, the hydrocarbon material is heavy fuel oil (HFO) with a sulphur content of up to about 12000 ppm.

In one embodiment, the oxidative desulphurisation process disclosed herein provides a HFO with a sulphur level of approx. 5000ppm or < 5000 ppm.

In one embodiment, the hydrocarbon material is clarified oil (slurry oil) with a sulphur content of up to about 16000 ppm.

15 In one embodiment, the oxidative desulphurisation process disclosed herein provides a clarified oil with a sulphur level of approx. 5000ppm or < 5000 ppm.

Three layers formed following oxidation of sulphur compounds

20 In one embodiment the process comprises contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system disclosed herein with stirring or agitation to provide an oxidised hydrocarbon mixture comprising oxidised sulphur compounds. Upon settling, the oxidised hydrocarbon mixture forms three layers comprising i) an aqueous layer , ii) a hydrocarbon layer containing the oxidised sulphur compounds, and iii) a layer containing the catalyst system.

25 Examples of hydrocarbon material that do result in the formation of 3 layers include diesel fuel, for example with a sulphur content of up to about 500 ppm, and gasoil, for example with a sulphur content of up to about 13000 ppm.

In one embodiment, the aqueous layer is separated. It may contain nonreacted ingredients such as oxidant, acid, Group VIb metal oxide and PTC.

In one embodiment, the hydrocarbon layer containing oxidised sulphur compounds is separated. A hydrocarbon stream with reduced sulphur content may be isolated by solvent extraction as described herein.

5 In one embodiment the layer containing the catalyst system is separated to provide a recovered catalyst system. The recovered catalyst system may be recycled as a catalyst system in a further oxidative desulphurisation process.

In one embodiment the further oxidative desulphurisation process forms a layer containing the catalyst system which is recycled in a further oxidative desulphurisation process as discussed below.

10 In one embodiment, visual observation is used to detect the layers. In one embodiment non visual techniques, as known in the art, are used to separate layers.

Cooling may be used to aid separation of the layers.

Two layers formed following oxidation of sulphur compounds

15 In one embodiment the process comprises contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system disclosed herein with agitation to provide an oxidised hydrocarbon mixture comprising oxidised sulphur compounds. Upon settling, the oxidised hydrocarbon mixture may form two layers comprising i) an aqueous layer and ii) a layer containing hydrocarbon, the oxidised
20 sulphur compounds, and the catalyst system.

Examples of hydrocarbon material that may result in the formation of 2 layers include, in some instances heavy fuel oil (HFO) with, for example, a sulphur content of up to about 12000 ppm.

Without being bound by theory, the inventors believe that heavy fuel oil does not
25 form 3 layers as the physical properties of the fuel are similar to the catalyst system. In some instances, HFO results in no layers being visually observed as discussed below, due to the physical characteristics of the material. For instance, the material may be dark and emulsified and/or suspended particles may be present.

The raffinate may be cooled to aid separation of layers. On a commercial scale,
30 non-visual techniques may be employed to separate layers.

In one embodiment, the aqueous layer is separated. It may contain nonreacted ingredients such as oxidant, acid, Group VIb metal oxide and PTC.

In one embodiment, the layer containing hydrocarbon, oxidised sulphur compounds and catalyst system is separated. A hydrocarbon stream with reduced sulphur content may be isolated by solvent extraction as described herein.

In one embodiment the layer containing the catalyst system is separated to provide a recovered catalyst system. The recovered catalyst system may be recycled as a catalyst system in a further oxidative desulphurisation process. The catalyst may be separated using known methodology including centrifuge, coalescer, gravity and other separation methods known to one skilled in the art.

In one embodiment the further oxidative desulphurisation process forms a layer containing the catalyst system which is recycled in a further oxidative desulphurisation process as discussed below.

No visually observable layers formed following oxidation of sulphur compounds

In one embodiment the process comprises contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system disclosed herein with agitation to provide an oxidised hydrocarbon mixture comprising oxidised sulphur compounds. Due to the physical nature of the hydrocarbon material, no layers may be visually observable. They may however, be detectable by instruments known in the art. In this situation, the oxidised sulphur compounds, the hydrocarbon material with reduced sulphur and the catalyst system may be separated by techniques such as distillation, (e.g. batch distillation) and solvent extraction. In one embodiment, solvent extraction is not carried out.

Examples of hydrocarbon material that may result in no visually observable layers include clarified oil (slurry oil), for example with a sulphur content of up to about 16000 ppm and HFO. Layers may be detectable by those skilled in the art.

In one embodiment, the layer containing hydrocarbon, water and oxidised sulphur compounds is separated from the catalyst system by evaporation.

In one embodiment, the layer containing hydrocarbon, water and oxidised sulphur compounds is separated from the catalyst system by solvent extraction.

In one embodiment the catalyst system is separated to provide a recovered catalyst system. The recovered catalyst system may be recycled as a catalyst system in a further oxidative desulphurisation process. When dealing with high viscosity oil containing sulphur, following the oxidation, the mixture may be distilled and the hydrocarbon
5 overhead with reduced sulphur content collected. The residue (still bottoms) containing the catalyst system may then be recycled.

Recycling of catalyst system

Following use of the catalyst system in a process of reducing the sulphur content
10 in a hydrocarbon material, the catalyst system can be recovered and recycled/reused *in situ* or after storage in further desulphurisation processes. This also advantageously contributes to reducing production costs and minimises environmental impact.

The present disclosure provides a process of recycling a catalyst system, as disclosed herein, which has been recovered following its use in an oxidative
15 desulphurisation process disclosed herein.

In one embodiment, the process of recycling the catalyst system disclosed herein comprises a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; b) allowing the oxidised hydrocarbon mixture
20 to settle to form a layer containing the catalyst system; and c) separating the catalyst system as a recovered catalyst system and recycling the recovered catalyst system by contacting the recovered catalyst system in the presence of hydrogen peroxide with a further hydrocarbon material containing sulphur compounds, for a period of time sufficient to oxidize at least a portion of the sulphur compounds to form an oxidised
25 hydrocarbon mixture.

In one embodiment, the process of recycling a catalyst system comprises: a) contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system disclosed herein with agitation for a period of time to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon
30 mixture; b) allowing the oxidised hydrocarbon mixture to settle for a sufficient period of time to form three layers: i) an aqueous layer, ii) a layer containing oxidised sulphur

compounds, and iii) a layer containing the catalyst system; c) separating the layer containing the catalyst system as a recovered catalyst system and d) recycling the recovered catalyst system by contacting the recovered catalyst system in the presence of aqueous hydrogen peroxide with a further hydrocarbon stream containing sulphur compounds, for a period of time sufficient to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture.

In one embodiment, the molar ratio of hydrogen peroxide to sulphur is about 2:1 to about 5:1, or about 2:1 to 2.5:1.

In one embodiment the layer containing the catalyst system in step b) is the middle layer or lower layer.

In one embodiment the oxidised hydrocarbon mixture, resulting from oxidative desulphurisation using the recovered catalyst system, is allowed to settle for a sufficient period of time to form three layers: i) an aqueous layer, ii) a layer containing hydrocarbons and oxidised sulphur compounds, and iii) a layer containing recovered catalyst system (recovered catalyst system layer).

The inventors have observed that the continual recycling of the layer containing the recovered catalyst system may result in the recovered catalyst system absorbing some oxidised sulphur in the form of sulphone such that the catalyst system increases in mass with each subsequent use. This may result in a slight decrease in the activity when the recovered catalyst system is reused. In order to maintain the activity of the recovered catalyst system for further use, it may be topped up with virgin (unused) catalyst.

In one embodiment the recovered catalyst system layer is topped up with virgin (unused) catalyst system prior to recycling. When to top up with virgin catalyst will be apparent to a person skilled in the art. In one embodiment the recovered catalyst system layer is topped up with virgin (e.g. freshly prepared or stored) catalyst system when the performance of the oxidation falls below the target level of sulphur content for each specific application. This is exemplified in the Examples.

In one embodiment the recovered catalyst system layer is recycled and reused up to 10 times, up to 7 times, or up to 5 times after its first use in the desulphurisation process before being replaced or topped up with virgin catalyst system. It is envisaged that when

the recovered catalyst system is topped up regularly with virgin catalyst system, that the recovered catalyst system could be recycled indefinitely.

In one embodiment the further oxidative desulphurisation process forms a layer containing a recycled catalyst system which is again recycled in a further oxidative
5 desulphurisation process.

Desulphurised hydrocarbon material identified by oxidised sulphur compounds formed in oxidative desulphurisation process

The process of reducing the sulphur content of a hydrocarbon material containing
10 sulphur compounds according to the process disclosed herein, involves the necessary step of oxidising at least a portion of the sulphur compounds contained in the hydrocarbon material in the presence of hydrogen peroxide and the catalyst system disclosed herein. The oxidation results in the formation of sulfoxide and/or sulphone compounds which are separated from the oxidised hydrocarbon mixture by known
15 techniques such as extraction and distillation as herein before described.

The presence of the sulfoxide and/or sulphone in the extractant serves as an effective way to identify a hydrocarbon material with low sulphur content produced using the process disclosed herein from other non-oxidative desulphurisation processes. In particular, the presence of sulfoxide and/or sulphone in the extractant of a
20 desulphurisation process would distinguish the process from, for instance, a hydrotreating/hydrorefining process where no such compounds are formed. In one aspect, there is provided a hydrocarbon material obtainable from the process for reducing the sulphur content of a hydrocarbon material containing sulphur compounds as disclosed herein.

25 In another aspect, there is provided a hydrocarbon material obtainable from the process for reducing the sulphur content of a hydrocarbon material containing sulphur compounds as disclosed herein, wherein sulphone and/or sulfoxide compounds are present in the extractant separated in the process.

In one embodiment, the hydrocarbon material is obtained from the process for
30 reducing the sulphur content of a hydrocarbon material containing sulphur compounds

as disclosed herein, wherein sulphone and/or sulfoxide compounds are present in the extractant separated in the process.

In one embodiment, there is provided a diesel fuel with a sulphur level of <15 ppm obtainable from the process for reducing the sulphur content of a diesel fuel containing sulphur compounds as disclosed herein, wherein sulphone and/or sulfoxide compounds are present in the extractant separated in the process.

In one embodiment, the diesel fuel has a sulphur level of < 10ppm.

Apparatus

Disclosed herein is an apparatus for reducing the sulphur content of a hydrocarbon stream containing sulphur compounds according to the process disclosed herein, the apparatus comprising: a) one or more oxidation reactors for oxidising at least a portion of the sulphur compounds in the hydrocarbon material containing sulphur compounds in the presence of the hydrogen peroxide and the catalyst system to provide the oxidised hydrocarbon mixture comprising hydrocarbon material, oxidised sulphur compounds and catalyst system; b) one or more vessels for delivering the hydrogen peroxide and the catalyst system to the oxidation reactor; c) a means for separating the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with reduced sulphur content; d) a means for separating the hydrocarbon stream with reduced sulphur content; e) a means for separating the catalyst system; f) one or more mixers for mixing the hydrocarbon stream with reduced sulphur content with an extraction solvent to extract oxidised sulphur compounds into the extractant; and g) means to separate the hydrocarbon material with reduced sulphur content.

The apparatus may further comprise a means for storing the separated catalyst system as a recovered catalyst system for further use in the process for reducing the sulphur content in a hydrocarbon material. The apparatus may further comprise a means for stirring or agitating the hydrocarbon material containing sulphur in the presence of the hydrogen peroxide and the catalyst system in the oxidation reactor.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the above-described embodiments, without departing from

the broad general scope of the present disclosure. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Figure 1 shows the general flow diagram of one embodiment of a process for reducing the sulphur content of a hydrocarbon material containing sulphur compounds (100) of the present disclosure and associated apparatus used in the process.

The process includes contacting a hydrocarbon material containing sulphur compounds, e.g. diesel, (111), hydrogen peroxide (112), and a catalyst system (113) as described herein in a reaction vessel, e.g. an oxidation reactor, (110) to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds (114). In some embodiments, the reaction vessel (110) is a Scheibel column. In some embodiments, the contacting is with stirring or agitation. In some embodiments, the diesel is heated to greater than about 60°C. In some embodiments, the oxidation reaction is carried out at a temperature (in °C) of between about 50 to about 150, between about 50 to about 100, between about 50 to about 80. In some embodiments, the oxidation reaction is carried out at a temperature (in °C) of about, or greater than about: 50, 60, 70, or 80.

The oxidised hydrocarbon mixture (114) is fed to a decanter (120). The decanter may be selected from any suitable process unit including, but not limited to, a liquid-liquid separator coalescer or settling vessel. In one embodiment, in the decanter (120) the oxidised hydrocarbon mixture settles to provide three layers comprising i) an aqueous layer, ii) a hydrocarbon layer containing the oxidised sulphur compounds, and iii) a layer containing the catalyst system. In another embodiment, in the decanter (120) the oxidised hydrocarbon mixture settles to provide two layers comprising i) an aqueous layer, ii) a layer containing hydrocarbon, the oxidised sulphur compounds, and the catalyst system. In another embodiment, in the decanter (120) the oxidised hydrocarbon mixture settles to provide a mixture comprising hydrocarbon, the oxidised sulphur compounds, and the catalyst system. In one embodiment, at least a portion of the layer containing the catalyst system is separated to provide a recovered catalyst system (122).

Following separation of the recovered catalyst system (122), at least a portion of the oxidised sulphur compounds is separated from the oxidised hydrocarbon mixture to provide a hydrocarbon material with a reduced sulphur content. In some

embodiments, the oxidised hydrocarbon mixture, following separation of catalyst, (121) is fed to a solvent extraction column (130) to undergo solvent extraction to provide a raffinate comprising the hydrocarbon material with reduced sulphur content (132) and an extract comprising the oxidised sulphur compounds (133), e.g. sulphoxides and sulphones. The solvent extraction is carried out with a first extraction solvent (131). In some embodiments, first extraction solvent (131) is selected from the group consisting of N-methyl pyrrolidone (NMP), acetonitrile, DMF, DMSO, methanol, water, brine, furfural and an ionic liquid solution or mixtures thereof, In some embodiments, the first extraction solvent (131) is a mixture of N-methyl pyrrolidone and water (aqueous NMP), In some embodiments, the first extraction solvent (131) is a mixture of about 98% N-methyl pyrrolidone and 2% water (2% aqueous NMP). In some embodiments the solvent extraction column (130) is a counter-current liquid-liquid extraction column.

The raffinate is fed to a vessel (140), e.g. a coalescer, a liquid-liquid extraction column, a static mixer or any other suitable process unit capable of mild liquid-liquid agitation, where it is washed with an aqueous solution (141) forming a washed stream. The washed stream (142) is fed to a separator (150) to form a washed hydrocarbon with reduced sulphur content (151) and a washate (152). The separator (150) may be selected from any suitable liquid-liquid separator known in the art.

In another embodiment, not shown in Figure 1, the vessel (140) and the separator (150) are a liquid-liquid extraction column. In one embodiment, water is used as a solvent in the liquid-liquid extraction column.

The extract (133) is fed to column (160) to where it is contacted with a second extraction solvent (161) to form a second extract (162). In some embodiments, the second extraction solvent (161) is selected from water, ethanol, methanol, ethylene glycol, trifluoroethanol, hexafluoroisopropanol, and combinations thereof. In one embodiment, the second extraction solvent (161) is water.

The second extract is fed to a separator (170) where at least a portion of a hydrocarbon material is separated from the second extract (162) to form a second further hydrocarbon material (172), being recovered hydrocarbon material, and a second extract depleted of hydrocarbon material (171).

The washate (152) is combined with the second extract depleted of hydrocarbon material (171) to form a combined stream (191). This combined stream is fed to a solvent recovery column (190) to obtain a stream comprising a portion of the first extraction solvent (193) e.g. NMP, a stream comprising a portion of the second extraction solvent (194) e.g. aqueous solution, and a residue stream (195). The solvent recovery column (190) may be selected from any suitable process unit, e.g. a distillation column.

The stream comprising a portion of the first extraction (193) is recycled to form at least a portion of the first extraction solvent (131). The stream comprising a portion of the second extraction solvent (194) is recycled to form a portion of aqueous solution (141) and/or the second extraction solvent (161).

The residue (195) is fed to a second light recovery column (200) to form a second light hydrocarbon stream (202) and a second heavy residue stream (203). The second light hydrocarbon stream (202) may be spilt into a first portion of the second light hydrocarbon stream (231) and a second portion of the second light hydrocarbon stream (232).

The second further hydrocarbon material (172) is fed to a light hydrocarbon recovery column (180) to form a light hydrocarbon stream (181), a heavy residue stream (183) and stream comprising a portion of the second further hydrocarbon material (182). In some embodiments the light hydrocarbon recovery column (180) may be selected from any suitable process unit, e.g. a distillation column. In some embodiments, the heavy residue stream is fed to the solvent recovery column (190) and/or the second light recovery column (200).

The light hydrocarbon stream (181) may be spilt and a first portion of the light hydrocarbon stream (211) and a second portion of the light hydrocarbon stream (212). The first portion of the light hydrocarbon stream (211) and the first portion of the second light hydrocarbon stream (231) may be combined with the stream comprising a portion of the second further hydrocarbon material (182) to form a recycle stream comprising the second further hydrocarbon material (221). The recycle stream comprising the second further hydrocarbon material (221) is combined with the oxidised hydrocarbon mixture (121).

In some embodiments, the recovered catalyst system (122) is recycled to form at least a portion of the catalysts system (113). In some embodiments, the catalysts system (113) comprises at least a portion of the recovered catalyst system (122) and fresh catalyst (243) obtained from the process described herein. In other embodiments, as shown in Figure 1, the recovered catalyst system (122) may be split into a recycled catalyst system stream (241) and a spent catalyst system (242). The recycled catalyst system stream (241) forms at least a portion of the catalysts system (113). In some embodiments, at least a portion of the spent catalyst system (242) is feed to the solvent recovery column (190) and/or the second light recovery column (200).

In the above process, known separators such as a coalescing, centrifugal or electrostatic type may be used.

In Figure 1, lines indicating the flow paths of: the portion of the first extraction (193); the portion of the second extraction solvent (194); and the at least a portion of the spent catalyst (242) have been omitted for clarity. The connectivity of these streams is represented by ●.

Products streams, including the hydrocarbon with reduced sulphur content (151), the light hydrocarbon streams (212, 232) and/or the second heavy residue stream (203) are recovered from the process described above. The person skilled in the art will appreciate that one or more of these product streams may be subjected to further refining by standard processes known in the art.

For example, the light hydrocarbon streams (212, 232) may be contacted, either separately or in some combination thereof, with an extractant, such as acetonitrile, to allow at least a portion of sulfoxide and/or sulphone compounds contained therein to be extracted into a sulfoxide and/or sulphone stream leaving a further low sulphur hydrocarbon stream. The sulfoxide and/or sulphone stream may be contacted with a further oxidant to give an aqueous sulphite stream and a low sulphur aromatic hydrocarbon stream, wherein the further oxidant oxidises sulphone and/or sulfoxide compounds to sulphite compounds.

Advantages of disclosed catalyst system in oxidative desulphurisation

The present disclosure provides a method of preparing a catalyst system for use in desulphurising hydrocarbon streams containing sulphur. Importantly, in some embodiments, the addition of hydrogen peroxide last in the process (or in the penultimate step) provides a surprisingly reactive catalyst system that is extremely efficient in the desulphurisation method. In addition, preparation of the catalyst uses significantly lower quantities of the Group VIb metal oxide, sodium tungstate, and oxidants such as hydrogen peroxide.

In contrast, previous methods for preparing catalysts used in desulphurization processes employ high amounts of Group VIb metal and hydrogen peroxide. Also, the order of addition of preparing known catalysts does not involve adding an oxidant in the last or penultimate step. Notably, the preparation of prior art catalysts known to the inventors involves a step of combining the oxidant with the metal oxide.

Prior art processes for preparing catalysts suitable for oxidative desulphurisation use a general methodology that involves the addition of an oxidant (e.g. hydrogen peroxide) early in the process. The prior art methodology exemplifies processes where an oxidant and metal salt oxide are stirred vigorously, followed by addition of a phosphorous acid or salt and a PTC. In some instances, an organic solvent is also present.

The inventors contemplated a number of disadvantages with preparing the catalyst according to the above general methodology and its subsequent use in an oxidative desulphurisation process when considering a commercial scale up. The noted disadvantages were based on economical, environmental and safety perspectives and include:

- the excess amounts of tungsten and hydrogen peroxide used is costly and requires consideration for wastewater disposal for environmental concerns economic loss;
- The addition of tungsten to hydrogen peroxide can potentially result in a violent reaction which has significant implications on a commercial scale and will be considered as a safety risk in a Hazard and Operability Study (HAZOP).

Other disadvantages associated with prior art catalysts and using large amounts of Group VIb metal such as tungsten, and hydrogen peroxide include: the excessive use of expensive metals; excessive use of hydrogen peroxide; potential safety hazard of uncontrollable exothermic reaction during catalyst formation; the use of a solvent to form

the catalyst; including the highly volatile and toxic solvents, handling losses and the need for storage of excessive amounts of transition metal, hydrogen peroxide and negative environmental impact if excessive amounts of transition metals find their way into aqueous waste streams or the product.

5 Amongst other differences, the catalyst system disclosed herein is prepared in an order of addition previously not contemplated by the prior art methodology such that the preparation of the catalyst system disclosed herein is commercially efficient, environmentally advantageous and forms a surprisingly reactive catalyst for oxidative desulphurisation.

10 In addition to the noted unusually high reactivity of the catalyst system disclosed herein, the use of the catalyst in the oxidative desulphurisation process disclosed herein results in a reduction in TAN as well as sulphur content in the hydrocarbon material being treated.

15 **EXAMPLE EMBODIMENTS**

1. A method of preparing a catalyst system, the method comprising combining a phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid.
2. The method of embodiment 1 wherein the oxidant is added last.
- 20 3 The method of embodiment 1 wherein the inorganic acid is added last.
4. A method of preparing a catalyst system, the method comprising
 - i) contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxides; followed by
 - ii) adding an inorganic acid to the mixture formed in i).
- 25 5. A method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising:
 - a phase transfer catalyst (PTC);
 - one or more metal oxide oxides; and
 - an inorganic acid.
- 30 6. The method of embodiment 5 wherein the one or more metal oxides is combined with the PTC prior to combining with the inorganic acid.

7. The method of embodiment 5 wherein the one or more metal oxides is added to the PTC.
8. The method of embodiment 5 wherein the PTC is added to the one or more metal oxides.
- 5 9. The method of embodiment 5 comprising:
- a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC;
 - b) adding the inorganic acid to the mixture of metal oxide and PTC followed by:
 - c) addition of the oxidant.
- 10 10. The method of embodiment 5 comprising:
- a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC;
 - b) adding the oxidant to the mixture of metal oxide and PTC followed by:
 - c) addition of the inorganic acid.
- 15 11. The method of any one of embodiments 1-10 wherein the one or more metal oxides is one or more Group VIb metal oxides.
12. The method of any one of embodiments 1-11 wherein the one or more metal oxides is one or more metal oxides is a Group VIb metal oxide in the form of a metal acid, metal trioxide, or a metal tetraoxide or salt thereof optionally as a hydrate.
- 20 13. The method of any one of embodiments 1-12 wherein the one or more metal oxide is selected from one or more of the following: tungstic acid, tungsten trioxide, tungstate salt including sodium tungstate, tungstate salt dihydrate including sodium tungstate dihydrate, molybdic acid, molybdic acid monohydrate, molybdic acid dihydrate, molybdenum trioxide, molybdate salt including sodium molybdate, and
- 25 molybdate salt dihydrate including sodium molybdate dihydrate.
14. The method of any one of embodiments 1-13 wherein the one or more metal oxides is a molybdate salt dihydrate, including sodium molybdate dihydrate, and/or a tungstate salt dihydrate, including sodium tungstate dihydrate.
15. The method of any one of embodiments 1-14 wherein the one or more metal
- 30 oxides is in an amount of 0.001 mole% of catalyst system to about 6 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst

system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system or about 0.3 mole% of catalyst system.

16. The method of any one of embodiments 1-15 wherein the metal oxide is sodium tungstate dihydrate.

5 17. The method of any one of embodiments 1-16 wherein the inorganic acid is a phosphorous containing inorganic acid.

18 The method of any one of embodiments 1-17 wherein the inorganic acid is selected from aqueous phosphoric, amino phosphonic acid or an acid including hydrochloric acid, sulfuric, acetic acid and other acids in combination with an inorganic
10 source of phosphorous, including sodium phosphate, potassium phosphate, sodium hydrogen phosphate, potassium hydrogen phosphate, sodium dihydrogen phosphate or potassium dihydrogen phosphate, wherein the resulting pH is less than 7.

19. The method of any one of embodiments 1-18 wherein the inorganic acid is aqueous phosphoric acid.

15 20. The method of any one of embodiments 1-19 wherein the inorganic acid is in an amount of about 0.001 mole% of catalyst system to about 6.0 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system or about 0.3 mol% of catalyst system.

20 21. The method of any one of embodiments 1-20 wherein the phase transfer catalyst (PTC) is selected from the group consisting of: quaternary ammonium salts; quaternary phosphonium salts; guanidinium salts, including hexaalkyl guanidinium salts; N-quaternized heterocyclic compounds, including pyridinium salts or imidazolium salts, phosphazanium salts and linear or cyclic polyethylene glycols and their ethers,
25 including cyclic crown ethers and cryptands.

22. The method of any one of embodiments 1-21 wherein the phase transfer catalyst (PTC) is a quaternary ammonium salt.

23 The method of any one of embodiments 1-22 wherein the phase transfer catalyst (PTC) is a quaternary ammonium salt selected from quaternary ammonium hydrogen
30 sulphates, quaternary ammonium chlorides and quaternary ammonium bromides.

24. The method of embodiment 23 wherein the quaternary ammonium salt comprises a cation selected from the group consisting of: methyl tricaprylyl ammonium, methyl trioctyl ammonium, methyl tridecyl ammonium, methyl tributyl ammonium, tetrabutyl ammonium, tetrapropyl ammonium, tetraethyl ammonium, methyl tridodecyl ammonium, octyl tributyl ammonium, dimethyl didecyl ammonium, hexadecyl trimethyl ammonium, stearyl trimethyl ammonium, tetraoctyl ammonium, tetrahexyl ammonium, hexadecyl tributyl ammonium, tetraoctadecyl ammonium, tetrabutyl phosphonium, trihexyl tetradecyl phosphonium, tetraoctyl phosphonium, cetyl pyridinium, hexabutyl guanidinium and other tetraalkyl ammonium and phosphonium cations, hexaalkyl guanidinium cations and alkyl pyridinium cations.
25. The method of embodiment 24 wherein the quaternary ammonium cation comprises a central nitrogen atom bound to four alkyl (hydrocarbyl) groups and has a total of at least 18 carbon atoms, or a range of 22 to 48 carbons atoms, or a range of 22 to 38 carbons atoms.
26. The method of embodiment 24 wherein the cation is methyltrioctyl ammonium, dimethyl didecyl ammonium, methyl tridecyl ammonium or a combination thereof.
27. The method of any one of embodiments 23-26 wherein the quaternary ammonium salt comprises an anion selected from the group consisting of phosphotungstate, oxophosphotungstate, phosphomolybdate, oxophosphomolybdate, chloride, bromide, hydrogen sulphate, methyl sulphate, sulphate, carbonate, hydrogen carbonate, methanesulfonate or a combination thereof.
28. The method of embodiment 27 wherein the anion is selected from the group consisting of chloride, bromide, hydrogen sulphate, methyl sulphate, sulphate, phosphotungstate, oxophosphotungstate or combinations thereof.
29. The method of embodiment 28 wherein the anion is chloride, bromide, hydrogen sulphate, a mixture of chloride and hydrogen sulphate or a mixture of bromide and hydrogen sulphate.
30. The method of any one of embodiments 1-29 wherein the PTC is didecyl dimethylammonium hydrogen sulphate (DDAHS) or didecyl dimethylammonium chloride (DDAC) or a mixture thereof.

- 31 The method of embodiment 30 wherein the PTC is didecyl dimethylammonium hydrogen sulphate (DDAHS) and didecyl dimethylammonium chloride (DDAC) in an anion ratio of about 80% hydrogen sulphate : 20% chloride.
- 32 The method of any one of embodiments 1-29 wherein the PTC is methyl tricaprylammonium hydrogen sulphate or methyl tricaprylammonium chloride or a mixture thereof.
- 33 The method of embodiment 32 wherein the PTC is methyl tricaprylammonium hydrogen sulphate and methyl tricaprylammonium chloride in an anion ratio of about 80% hydrogen sulphate : 20% chloride.
34. The method of embodiment 31 wherein the PTC is an aqueous solution.
35. The method of any one of embodiments 1-34 wherein the PTC is in an amount of about 2.5 mole% of catalyst system to about 3.5 mole % of catalyst system; or about 3.0 mole% of catalyst system to about 3.3 mole % of catalyst system or about 3.2 mole % of catalyst system.
36. The method of any one of embodiments 1-35 wherein the oxidant is an aqueous solution.
37. The method of any one of embodiments 1-36 wherein the oxidant is about 20-70% aqueous hydrogen peroxide, or about 50% aqueous hydrogen peroxide.
38. The method of any one of embodiments 1-37 wherein the oxidant used in preparing the catalyst system is in a molar ratio of oxidant to metal oxide in the range of about 7000:1 to 100:1; or about 7000:1 to 300:1 or about 500:1.
- 39 The method of any one of embodiments 1-38 wherein the molar ratio of PTC to oxidant used in preparing the catalyst system is about 0.02:1 to 0.05:1; or about 0.03:1.
40. The method of any one of embodiments 1-39, wherein the molar ratio of metal oxide to PTC is in a range of about 0.5:1 to 0.0004:1; or about 0.18:1 to 0.005:1 or about 0.09:1.
41. The method of any one of embodiments 1-40, wherein the molar ratio of PTC to metal oxide to inorganic acid to oxidant is in a range of about 0.032 : 0.0057 : 0.0055 : 0.96 to about 0.032 : 0.00015 : 0.00028 : 0.97 or about 0.032 : 0.0029 : 0.0028 : 0.96.

42. The method of any one of embodiments 1-41 wherein the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid to form a reaction mixture.
43. The method of embodiment 42 wherein the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid to form a reaction mixture comprising an oxidised catalyst mixture.
44. The method of any one of embodiments 1-42, wherein the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid and agitated for a period of time to form an oxidised catalyst mixture.
45. The method of embodiment 44 wherein agitation occurs for at least about 1 sec to at least about 30 min including, at least about, 1s, 5s, 10s, 20s, 30s, 40s, 50s, 1 min, 5, min, 10 min, 15 min or 30 minutes.
46. The method of embodiment 44 or 45, wherein multiple layers form following settling of the oxidised catalyst mixture.
47. The method of embodiment 46 wherein one or more water immiscible layers and an aqueous layer form.
48. The method of any one of embodiments 43-47 wherein two layers form.
49. The method of embodiment 47 or 48 wherein a water-immiscible layer forms comprising the oxidised catalyst mixture.
50. The method of any one of embodiments 47 - 49 wherein a water-immiscible layer forms comprising the catalyst system.
51. The method of any one of embodiments 47-50 wherein the water-immiscible layer is separated to form a separated water-immiscible layer.
52. The method of any one of embodiments 43-47 wherein three layers form.
53. The method of embodiment 52 wherein two water immiscible layers and an aqueous layer form.
54. The method of embodiment 53 wherein one water immiscible layer comprises the catalyst system and one water immiscible layer comprises an organic material such as hydrocarbons.

55. The method of any one of embodiments 52 -54 wherein the PTC is a mixture of methyltricaprylyl ammonium hydrogen sulphate and methyltricaprylyl ammonium chloride dissolved or suspended in hydrocarbon (e.g. diesel).
56. The method of any one of embodiments 43 – 55 wherein a water-immiscible
5 layer comprising the catalyst system is separated from the oxidised catalyst mixture and stored for future use.
57. The method of embodiment 56 wherein the water immiscible layer comprising the oxidised catalyst system is stored for up to about 3 years, or 2 years or 1 year or 6 months or 3 months for future use.
- 10 58. A method of preparing a catalyst system, the method comprising the steps of:
a) combining sodium tungstate dihydrate and an aqueous quaternary ammonium salt to form a metal oxide and quaternary ammonium salt mixture;
b) adding aqueous phosphoric acid to the metal oxide and quaternary ammonium salt mixture-to form a reaction mixture; followed by
15 c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst mixture;
d) allowing the oxidised catalyst mixture to settle to form multiple layers including a water-immiscible layer containing the catalyst system; and
e) optionally separating the water immiscible layer containing the catalyst
20 system.
59. The method of preparing a catalyst system according to embodiment 58, the method comprising the steps of:
a) combining sodium tungstate dihydrate and aqueous didecyl
dimethylammonium hydrogen sulphate (DDAHS) to allow dissolution of the sodium
25 tungstate dihydrate in DDAHS to form a dissolved metal solution;
b) adding aqueous phosphoric acid to the dissolved metal solution; followed by
c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst solution;
d) allowing the oxidised catalyst solution to settle to form 2 layers including a
30 water-immiscible layer containing the catalyst system; and

e) optionally separating the water-immiscible layer containing the oxidised catalyst solution.

60. The method of preparing a catalyst system according to embodiment 58, the method comprising the steps of:

- 5 a) combining sodium tungstate dihydrate and a mixture of methyl tricaprylammonium hydrogen sulphate and methyl tricaprylammonium chloride dissolved or suspended in hydrocarbon (e.g. diesel) to form a reaction mixture;
- b) adding aqueous phosphoric acid to the reaction mixture; followed by
- c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst
10 solution;
- d) allowing the oxidised catalyst solution to settle to form 3 layers including a water-immiscible layer containing the catalyst system; and
- e) optionally separating the water-immiscible layer containing the oxidised catalyst solution.
- 15 61. The method of any one of embodiments 58-60 wherein steps a) - d) are carried out at ambient temperature.
- 62 The method of any one of embodiments 58-60 wherein in step c) the aqueous hydrogen peroxide is added and mixed for about 30 minutes.
- 63 The method of any one of embodiments 58-60 wherein in step d) the oxidised
20 catalyst solution is allowed to settle for a period of time in a range of about 1 to 10 minutes.
64. A catalyst system prepared by the method of anyone of embodiments 1-63.
65. The catalyst of embodiment 64 for use in a process of desulphurising a hydrocarbon material containing sulphur.
- 25 66. A process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds, the process comprising:
- a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system prepared by the method of any one of
embodiments 1-63, so as to oxidise at least a portion of the sulphur compounds in the
30 hydrocarbon material to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and

- b) separating at least a portion of the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with a reduced sulphur content.
67. The process of embodiment 66 wherein the catalyst system is added to the hydrocarbon material followed by addition of the hydrogen peroxide.
68. The process of embodiment 66 wherein the catalyst system and hydrogen peroxide are added simultaneously to the hydrocarbon material.
69. The process of embodiment 66 wherein the catalyst system is added to a mixture of the hydrocarbon material and the hydrogen peroxide
70. The process of any one of embodiments 66-69 wherein the hydrocarbon material, hydrogen peroxide and the catalyst system are mixed together with agitation.
71. The process of any one of embodiments 66-70 wherein the hydrocarbon material is heated to about 60°C, prior to or during agitation.
72. The process of any one of embodiments 66-71 wherein the catalyst system used in the process is contained in the oxidised catalyst mixture.
73. The process of any one of embodiments 66-72 wherein the catalyst system used in the process is contained in the water-immiscible layer.
74. The process of embodiment 73 wherein the catalyst system is not isolated from the water-immiscible layer.
75. The process of any one of embodiments 66-71 wherein the catalyst system is prepared and used in the process *in situ*.
76. The process of any one of embodiments 66-75 wherein the molar ratio of hydrogen peroxide to sulphur in hydrocarbon material containing sulphur compounds is in a range of about 2:1 to about 5:1 or about 2:1 to about 2.5:1.
77. The process of any one of embodiments 66-75 wherein the molar ratio of hydrogen peroxide to sulphur in hydrocarbon material containing sulphur is about 2.5:1.
78. The process of any one of embodiments 66-75 wherein the mass ratio of catalyst system disclosed herein to sulphur in hydrocarbon material containing sulphur (catalyst:S) is about 0.2:1.

79. The process of any one of embodiments 66-78 wherein the at least a portion of the oxidised sulphur compounds is separated from the oxidised hydrocarbon mixture by solvent extraction to provide a raffinate comprising the hydrocarbon material with reduced sulphur content and an extract comprising the oxidised sulphur compounds.
- 5 80. The process of embodiment 79 wherein the hydrocarbon material with reduced sulphur content is contacted with an extractant to allow further oxidised sulphur to be extracted into the extractant.
81. The process of embodiment 66-80 wherein the extraction is carried out with a polar extractant selected from the group consisting of N-methyl pyrrolidone (NMP),
10 acetonitrile, DMF, DMSO, methanol, water, brine, furfural and an ionic liquid solution or mixtures thereof.
82. The process of embodiment 80 or 81 wherein the extractant is a mixture of N-methyl pyrrolidone and water (aqueous NMP), preferably as a mixture of about 98% N-methyl pyrrolidone and 2% water (2% aqueous NMP).
- 15 83. The process of any one of embodiment 66-82 wherein the hydrocarbon stream with reduced sulphur content is washed with an aqueous solution including water and brine to form a washed hydrocarbon with reduced sulphur content and a washate.
- 84 The process of any one of embodiments 66-83 wherein the hydrocarbon stream containing sulphur compounds has a sulphur mass of greater than about 200 ppm, 300
20 ppm, 500 ppm, 1000 ppm, or 5000 ppm
85. The process of any one of embodiments 66-83 wherein the hydrocarbon stream containing sulphur compounds has a sulphur mass of less than about 15,000 ppm, 12,000 ppm, 5000 ppm, 1000 ppm or 500 ppm.
86. The process of any one of embodiments 66-85 wherein the hydrocarbon stream
25 containing sulphur compounds is selected from diesel, clarified oil (including slurry oil), heavy fuel oil (HFO), light cycle oil, recycled base oil and natural gas liquids.
87. The process of any one of embodiments 66-86 the process comprises
contacting the hydrocarbon stream containing sulphur compounds with
hydrogen peroxide and the catalyst system with stirring or agitation to provide the
30 oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and

allowing the oxidised hydrocarbon mixture to settle to provide three layers comprising i) an aqueous layer, ii) a hydrocarbon layer containing the oxidised sulphur compounds, and iii) a layer containing the catalyst system.

5 88. The process of embodiment 87 wherein the hydrocarbon material containing the sulphur compounds is diesel or gasoil.

89. The process of any one of embodiments 66-88 the process comprises contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system with stirring or agitation to provide the oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and
10 allowing the oxidised hydrocarbon mixture to settle to provide two layers comprising i) an aqueous layer, ii) a layer containing hydrocarbon, the oxidised sulphur compounds, and the catalyst system.

90. The process of any one of embodiments 66-88 the process comprises contacting the hydrocarbon stream containing sulphur compounds with
15 hydrogen peroxide and the catalyst system with stirring or agitation to provide the oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and allowing the oxidised hydrocarbon mixture to settle to provide a mixture comprising hydrocarbon, the oxidised sulphur compounds, and the catalyst system.

91. The process of embodiment 90 wherein no separate layers are visually
20 observable after settling.

92. The process of any one of embodiments 89 – 91 wherein the hydrocarbon material containing the sulphur compounds is heavy fuel oil.

93. The process of any one of embodiments 87 -89 wherein the layer containing the catalyst system is separated to provide a recovered catalyst system.

25 94. The process of embodiment 90 or 91 wherein the catalyst system is separated to provide a recovered catalyst system.

95. The process of embodiment 93 or 94 wherein the recovered catalyst system is recycled as a catalyst system in a further oxidative desulphurisation process.

96. The process of embodiment 95 wherein the further oxidative desulphurisation
30 process forms a layer containing the catalyst system which is recycled in a further oxidative desulphurisation process.

97. The process of any one of embodiments 66-78 the process comprises contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system with agitation to provide the oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and
- 5 separating the oxidised sulphur compounds, the hydrocarbon material with reduced sulphur and the catalyst system by distillation, including batch distillation.
98. The process of embodiment 97 wherein the hydrocarbon material containing the sulphur compounds is clarified oil including slurry oil or HFO.
99. A hydrocarbon material obtainable from the process for reducing the sulphur
- 10 content of a hydrocarbon material containing sulphur compounds according to any one of embodiments 66-97.
100. A hydrocarbon material obtainable from the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to any one of embodiments 66-98, wherein the hydrocarbon material has a reduced sulphur
- 15 content and TAN (total acid content) relative to the hydrocarbon material containing sulphur compounds.
101. A process of recycling the catalyst system used in the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to any one of embodiments 66-98.
- 20 102. The process of recycling the catalyst system according to embodiment 101 comprising: a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; b) allowing the oxidised hydrocarbon mixture to settle to form a layer containing the catalyst system; and c) separating the catalyst
- 25 system as a recovered catalyst system and recycling the recovered catalyst system by contacting the recovered catalyst system in the presence of hydrogen peroxide with a further hydrocarbon material containing sulphur compounds, for a period of time sufficient to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture.
- 30 103. The process of recycling the catalyst system according to embodiment 101 or 102 comprising:

a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system for a period of time to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds;

5 b) allowing the oxidised hydrocarbon mixture to settle for a sufficient period of time to form three layers: i) an aqueous layer, ii) a hydrocarbon layer containing oxidised sulphur compounds, and iii) a layer containing catalyst system; and

 c) separating the layer containing the catalyst system as a recovered catalyst system and recycling the recovered catalyst system by contacting the recovered catalyst
10 system and hydrogen peroxide with a further hydrocarbon material containing sulphur compounds, for a period of time sufficient to oxidize at least a portion of the sulphur compounds to form an oxidised hydrocarbon mixture.

104. The process according to any one of embodiments 101-103 wherein the molar ratio of hydrogen peroxide to sulphur is in a range of about 2:1 to about 5:1 or about
15 2:1 to 2.5:1.

105. The process of embodiment 103 wherein the layer containing the catalyst system in step b) is the middle layer or lower layer.

106 The process of embodiment 102 or 103 wherein the oxidised hydrocarbon mixture produced in c), is allowed to settle for a sufficient period of time to form three
20 layers: i) an aqueous layer, ii) a layer containing hydrocarbons and oxidised sulphur compounds, and iii) a layer containing recovered catalyst system..

107. The process according to embodiment 106 wherein the recovered catalyst system absorbs oxidised sulphur in the form of sulphone such that the catalyst system increases in mass.

25 108. The process according to embodiment 107 wherein the recovered catalyst system is replenished with freshly prepared catalyst system.

109. The process according to embodiment 108 wherein the recovered catalyst system is recycled up to 2-10 times after its first use in the desulphurisation process before being replaced or topped up with freshly made catalyst system.

110. An apparatus for reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to the process of any one of embodiments 66-109, the apparatus comprising:
- a) one or more oxidation reactors for oxidising at least a portion of the sulphur compounds in the hydrocarbon material containing sulphur compounds in the presence of the hydrogen peroxide and the catalyst system to provide the oxidised hydrocarbon mixture comprising hydrocarbon material, oxidised sulphur compounds and catalyst system;
 - b) one or more vessels for delivering the hydrogen peroxide and the catalyst system to the oxidation reactor;
 - c) a means for separating the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with reduced sulphur content;
 - d) a means for separating the hydrocarbon stream with reduced sulphur content;
 - e) a means for separating the catalyst system;
 - f) one or more mixers for mixing the hydrocarbon material with reduced sulphur content with an extraction solvent to extract oxidised sulphur compounds into the extractant; and
 - g) means to separate the hydrocarbon material with reduced sulphur content.
111. The apparatus of embodiment 110 wherein the apparatus further comprises a means for storing the separated catalyst system as a recovered catalyst system for further use in the process for reducing the sulphur content in a hydrocarbon material.
112. The apparatus of embodiment 110 wherein the apparatus further comprises a means for stirring or agitating the hydrocarbon material containing sulphur in the presence of the hydrogen peroxide and the catalyst system in the oxidation reactor.
113. The method of embodiment 44 or embodiment 45, wherein the catalyst system is not further isolated from the oxidised catalyst mixture.
114. The process of embodiment 79 wherein the solvent extraction is carried out with a first extraction solvent selected from the group consisting of N-methyl pyrrolidone (NMP), acetonitrile, DMF, DMSO, methanol, water, brine, furfural and an ionic liquid solution or mixtures thereof.

115. The process of embodiment 114 wherein the first extraction solvent is a mixture of N-methyl pyrrolidone and water (aqueous NMP), preferably as a mixture of about 98% N-methyl pyrrolidone and 2% water (2% aqueous NMP).
116. The process of embodiment 79 wherein the process further comprises contacting
5 the extract comprising the oxidised sulphur compounds with a second extraction solvent to form a second extract.
117. The process of embodiment 116 wherein the second extraction solvent is selected from water, ethanol, methanol, ethylene glycol, trifluoroethanol, hexafluoroisopropanol, and combinations thereof.
- 10 118. The process of embodiment 116 or embodiment 117 wherein the second extraction solvent is water.
119. The process of any one of embodiments 116 to 118, wherein the process further comprises separating at least a portion of a hydrocarbon material from the second extract to form a second further hydrocarbon material and a second extract depleted of
15 hydrocarbon material.
120. The process of embodiment 119, wherein the process further comprises recycling the second further hydrocarbon material.
121. The process of embodiment 120, wherein the process comprises combining the second further hydrocarbon material with the oxidised hydrocarbon mixture comprising
20 oxidised sulphur compounds prior to step b) of embodiment 66.
122. The process of any one of embodiments 119 to 121, wherein the process further comprises separating at least a portion of the first extraction solvent and/or the second extraction solvent from the second extract depleted of hydrocarbon of embodiment 119 to form one or more separated extraction solvent streams and a residue stream.
- 25 123. The process of embodiment 122, wherein the process further comprises separating at least a portion of the hydrocarbon material from the residue of embodiment 122 to form a light hydrocarbon stream and a second residue.
124. The process of embodiment 123, wherein the separating at least of portion of the hydrocarbons from the residue is achieved by distillation.
- 30 125. The process of embodiment 122, wherein a first separated extraction solvent stream is formed comprising at least a portion of the first extraction solvent.

126. The process of any one of embodiments 122 to 125, wherein a second separated extraction solvent stream is formed comprising at least a portion of the second extraction solvent.
127. The process of any one of embodiments 122 to 126 wherein at least a portion of
5 one or more of the one or more separated extraction solvent streams is recycled.
128. The process of embodiment 127 wherein at least a portion of the first separated extraction solvent streams is recycled as at least portion of the extraction solvent of embodiment 79.
129. The process of embodiment 123 or embodiment 124 wherein the light
10 hydrocarbon stream is combined with the second further hydrocarbon material of embodiment 119.
130. The process of embodiment 123 wherein the light hydrocarbon stream is further processed.
131. The process of embodiment 130 wherein the further processing comprises one
15 or more of solvent extraction and desulphonylation.
132. The process of embodiment 83, wherein the washate is combined with the second extractant depleted of hydrocarbon prior to the separating of embodiment 122.
133. The process of embodiment 93 or embodiment 94 wherein at least a portion of the recovered catalyst system is combined with the residue of claim 122.
- 20 134. The process of embodiment 93 or embodiment 94 wherein at least a portion of the recovered catalyst system is combined with the second residue of embodiment 123.
135. A method of preparing a catalyst system, the method comprising combining one or more phase transfer catalysts (PTC), one or more metal oxides; one or more oxidants and one or more inorganic acids, wherein the method does not comprise combining the
25 oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or inorganic acid are also present in the mixture.
136. The method of embodiment 135, wherein the PTC and the oxidant are combined followed by addition of the metal oxide and then addition of the inorganic acid.
137. The method of embodiment 135, the method comprising combining a phase
30 transfer catalyst (PTC) and one or more metal oxides; followed by addition of an oxidant and an inorganic acid.

EXAMPLES

In the Examples, the inventors compare the catalyst system disclosed herein and its use in oxidative desulphurisation with a baseline catalyst prepared with the same starting material but in an order according to the known methodology.

Specifically, the catalyst used in the baseline run discussed below in Example 1 was prepared using a general procedure that reflects the known methodology.

The inventors also compared the efficiency of the catalyst system disclosed herein with an example from experiments disclosed in the prior art (US Patent 7,744,749, hereinafter US '749, (Example 1)). Comparisons with prior art catalysts and the catalyst system disclosed herein are detailed in Example 11.

In the following Examples (Examples 2-11), the catalyst system of the present disclosure, its preparation and use in oxidatively desulphurising hydrocarbon streams is outlined and compared with known methodologies.

Materials

The availability of the compounds used in the Examples is as follows:

Compound	CAS #	Availability
BTC 1010-80% Didecyldimethylammonium chloride (DDAC)	7173-51-5	Stepan
Sodium Tungstate Dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$)	10213-10-2	Sigma-Aldrich
Hydrogen Peroxide (35% H_2O_2)	7722-84-1	Solvay
Phosphoric acid solution (81%)	7664-38-2	Sigma-Aldrich
N-Methyl-2- Pyrrolidone (NMP)	872-50-4	Sydney Solvents
Sulphuric Acid	7664-93-9	Australian Chemical Reagents
Methyl Tricaprylyl Ammonium Hydrogen Sulphate/Chloride	355009-64-2	produced using a proprietary method under licence from Ultraclean Technology
Didecyl Dimethylammonium Hydrogen Sulphate/chloride (DDAHS/DDAC)	-	DDAHS is available from China.cn. DDAC is available from Seqens, Lonza, Stepan and is converted

		to a mixture of DDAC/DDHS as outlined in Example 7.
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In the Examples, where indicated, the sulphur content in the hydrocarbon material was measured to ASTM D5623 or ASTM D4294 before and after the oxidative process using an XPLOER TN/TS for Total Nitrogen by Chemiluminescence and Total Sulfur
5 by UV-Fluorescence, manufactured by Trace Elemental Instruments for ASTM D5623 and an SLFA-6000 X-ray Fluorescence Sulfur-in-Oil Analyzer, manufactured by Horiba for ASTM D4294.

Comparative Example 1: Preparation of baseline catalyst and oxidation (#290)

10 Using the general methodology of the prior art, a catalyst was prepared and used as a baseline for the inventors to study the effectiveness of the catalysts system disclosed herein when used in oxidative desulphurisation reactions.

As noted above the general methodology adopted by the prior art (e.g. as disclosed in US '749 (Example 1) and US 8,394,735, hereinafter '735, (Example 1)) involves an
15 order of addition of the ingredients where the oxidant is added early in the process of preparing the catalyst. The preparation of the baseline catalyst uses the following ingredients: sodium tungstate dihydrate, didecyldimethyl ammonium hydrogen sulphate/chloride, phosphoric acid and aqueous hydrogen peroxide in an order of addition that required the hydrogen peroxide to be present first in the preparation process
20 and combined with hydrogen peroxide. The preparation process is described below.

The baseline catalyst was pre-prepared at room temperature in the following manner:

- 1) 0.32g (0.001068 moles) of Na₂WO₄·2H₂O was added to 9.1g (0.0936 moles) of 35% H₂O₂ in a beaker and gently agitated by hand for 10 minutes and dissolved in the
25 H₂O₂;
- 2) 0.12g (0.000992 moles) of H₃PO₄ (81%) was added to the mixture formed in step 1); and gently agitated by hand for 10 minutes and dissolved in the mixture; and

3) 0.6g (0.00106 moles) of DidecylDimethylAmmonium with an estimated anion ratio of 80% Hydrogen Sulphate to 20% Chloride (DDAHS/DDAC) was then added to the mixture formed in step 2).

At this stage, it is possible to use the resulting catalyst mixture containing the catalyst system without further processing to separate or purify the catalyst system. Alternatively, the catalyst layer is separated from the catalyst mixture according to the following.

The catalysts was decanted, with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for about 48 hours. The aqueous phase was drained to recover the organic catalyst layer (1.17g).

The present inventors used the above separated baseline catalyst layer in a process for oxidatively desulphurising a hydrocarbon stream which involved the following steps.

Transmix diesel

A transmix diesel was used as the baseline diesel and as the diesel in a number of comparative oxidative desulphurisation reactions using the baseline catalyst and the catalysts system disclosed herein. This was available in a single drum and thereby avoided the potential variability of samples from multiple drums.

Oxidation using transmix and baseline catalyst

A 2kg sample of diesel (transmix) was checked for sulphur and nitrogen to ASTM D5623. The diesel sample contained 280ppm sulphur and 8.29 ppm nitrogen. The mass ratio of baseline catalyst to sulphur was calculated as 0.214:1. The molar ratio of H₂O₂ per Mole Sulphur was calculated as 5.362.

The diesel sample was pre heated to >60°C and transferred into a beaker containing the baseline catalyst mixture, which was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first and measured as 3.1g. An organic layer of

recovered baseline catalyst was then observed and removed and measured as 1.17g. The oxidised diesel was then recovered and measured sulphur of 235.8ppm.

The oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon (diesel) ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This first extraction step (Strip #1) was repeated with the diesel sample for 12 more time until strip #13.

The final step was to remove residual solvent using a water wash. The demineralised water was added at a ratio of 0.05:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes (ww#1). This step was repeated 3 more times until ww#4.

The sample was then checked for sulphur and nitrogen. The sulphur was 5.95 ppm and nitrogen was 4.16 ppm.

15 Figure 2

The baseline (#290) is shown in Figure 2. Figure 2 depicts the initial reduction of sulphur in the transmix diesel following oxidation using the baseline catalyst from 280 ppm to 235 ppm. This is further reduced following solvent extraction with water/NMP (0.5:1), with the sulphur content reaching 11.28 ppm after 13 solvent extractions (strip13). Washing with water (x4) further reduced the sulphur content to 5.95 ppm.

Example 2 (#311)

Catalyst

A catalyst system according to the present disclosure was pre-prepared at room temperature in the following manner:

- 1) 91.61g (0.147 Moles) of methyl tricaprylyl ammonium with an estimated anion ratio of 80% Hydrogen Sulphate to 20% Chloride was measured in a beaker.
- 2) 4.82g (0.0146 Moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by hand for 10 minutes.
- 30 3) 1.75g (0.0145 Moles) of H_3PO_4 (81%) was added to the mixture of 2) and gently agitated by hand for 10 minutes.

- 4) 357.29g (5.252 Moles) of 50% H₂O₂ was then added to 3).
- 5) The resulting solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 451.89g

- 5 The sample was then decanted, with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst layer was recovered was 104.3g.

10 Oxidation

A 2kg sample of transmix diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280ppm sulphur and 8.29 ppm nitrogen.

The sample was pre heated to >60°C and placed under the mixer.

- 0.16g of the catalyst layer formed above was added to the diesel sample, followed
15 by 2.86g 50% H₂O₂. The solution was then mixed for 30 minutes at 6000 rpm.

The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. An organic layer of recovered catalyst was then observed and removed. The oxidised diesel was then recovered and measured sulphur of 132.25 ppm.

- 20 A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This step was repeated 9 more times.

- The final step was to remove residual solvent using a water wash. The
25 demineralised water was added at a ratio of 0.05:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes. This step was repeated once.

The sample was then checked for sulphur and nitrogen. The sulphur was 3.19 ppm and nitrogen was 7.73 ppm.

30 Exemplary calculation of ratio of moles of O:S in oxidation reaction:

H₂O₂ (50%) – 2.86g

H_2O_2 (100%) – 1.43g

Catalyst layer – 0.16g

Molecular weight: S=32, O=16, H_2O_2 =34

Mass feed= 2000g

5 Sulphur = 280ppm

Mass sulphur = $2000(280/1000000)$

=0.560g

Mass oxygen = $1.43(16/34)$ (based on oxygen content of H_2O_2)

10 =0.67g

Moles of S (32g/mol) = $0.560/32 = 0.0175$ moles

Moles of O (16 g/mol) = 0.042 moles

15 Therefore, the ratio of O:S is 0.042:0.0175 i.e about 2.41 (Target stoichiometry =2.5)

Example 3 (#301-CLO 99% W reduction, distillation)

Catalyst:

A catalyst system according to the present disclosure was pre-prepared at room
20 temperature in the following manner;

1) 100.11g (0.177 moles) of didecyl dimethyl ammonium with an estimated anion
ratio of 80% Hydrogen Sulphate to 20% Chloride was measured in a beaker.

2) 0.526g (0.00159 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by
hand for 10 minutes.

25 3) 0.186g (0.00154 moles) of H_3PO_4 (81%) was added to the mixture of 2) and gently
agitated by hand for 10 minutes.

4) 517.52g (5.325 moles) of 35% H_2O_2 was then added to 3).

5) The solution was then mixed using a Silverstone L5M-A mixer at room
temperature for 30 minutes.

30 Post mixing the mass was checked at 615.78g

The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst layer recovered was 159.27g.

5

Oxidation

1001g sample of clarified oil (slurry oil) was checked for sulphur to ASTM D4294. The sample was 15424.6 ppm sulphur.

The sample was pre heated to $>60^{\circ}\text{C}$ and placed under the mixer.

10 3.8g of catalyst layer was added, followed by 94.1g 50% H_2O_2 . The solution was then mixed for 30 minutes at 6000 rpm.

1079.3g of the sample was then distilled in a small vacuum batch distillation unit with heated condenser. The recovered overhead yield was 66.84%, with bitumen cutter stock residue recovered yield of 16.28% with loss of 16.88%. The overhead recovered sulphur was 4376.75 ppm. This surpassed the 5000 ppm target.

15

Example 4 (#308 –HFO)

Catalyst:

A catalyst system according to the present disclosure was pre-prepared at room temperature in the following manner (as per Example 3);

- 1) 100.11g (0.177 moles) of didecyl dimethyl ammonium with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 2) 0.526g (0.00159 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added and gently agitated by hand for 10 minutes.
- 25 3) 0.186g (0.00154 moles) of H_3PO_4 (81%) was added to the mixture and gently agitated by hand for 10 minutes.
- 4) 517.52g (5.325 moles) of 35% H_2O_2 was then added.
- 5) The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

30 Post mixing the mass was checked at 615.78g

The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst layer recovered was 159.27g.

5

Oxidation

1007.60g sample of #6 Heavy Fuel Oil (HFO) was checked for sulphur to ASTM D4294 The sample was 11407ppm sulphur.

The sample was pre heated to $>60^{\circ}\text{C}$ and placed under the mixer.

10 1.91g of catalyst layer was added, followed by 46.14g 50% H_2O_2 . The solution was then mixed for 30 minutes at 8000 rpm. After settling, visual observation of the layers was difficult.

15 A sample of HFO was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done on a stirred heated mixer at $>80^{\circ}\text{C}$ for a minimum of 10 minutes. The sample was then allowed to cool and settle in a refrigerated container. The solvent was then removed. This step was repeated a further 6 times.

20 The final step was to remove residual solvent using a single water wash. The demineralised water was added at a ratio of 1.5:1 water to HFO and was mixed on a stirred heated mixer at $>80^{\circ}\text{C}$ for a minimum of 10 minutes. The sample was then allowed to cool and settle in a refrigerated container. The aqueous phase was then removed.

The sample was then checked for sulphur. The sulphur was 2043.43 ppm. This surpassed the target of 5000 ppm.

25 **Example 5** (#304 -diesel 500 ppm)

Catalyst:

A catalyst system according to the present disclosure was pre-prepared at room temperature in the following manner;

1) 61.32g (0.109 moles) of didecyl dimethyl ammonium with an estimated anion
30 ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.

- 2) 6.44g (0.0195 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by hand for 10 minutes.
- 3) 2.29g (0.0189 moles) of H_3PO_4 (81%) was added to the mixture formed in step 2) and gently agitated by hand for 10 minutes.
- 5 4) 316.99g (3.262 moles) of 35% H_2O_2 was then added to the mixture of step 3).
- 5) The solution of 4) was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 381.47g

- The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst layer recovered was 101.69g.

Oxidation

- 15 877.61g sample of diesel was checked for sulphur and nitrogen to ASTM D4294. The sample contained 483.1ppm sulphur and 15.97ppm nitrogen.

The sample was pre heated to $>60^\circ\text{C}$ and placed under the mixer.

0.21g of the catalyst was added, followed by 2.01g 50% H_2O_2 . The solution was then mixed for 30 minutes at 6000rpm.

- 20 The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. An organic layer of recovered catalyst was then observed and removed. The oxidised diesel was then recovered and measured sulphur of 258.54 ppm

About 868.81g diesel was recovered.

- 25 A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This step was repeated a further 8 times.

- The final step was to remove residual solvent using two water washes. The demineralised water was added at a ratio of 0.05:1 water to diesel and shaken in a

separatory funnel at room temperature for 2 minutes. This step was repeated until reaching a terminal value (no further sulphur reduction).

The sample was then checked for sulphur and nitrogen. The sulphur was 6.52 ppm and nitrogen was 3.74 ppm.

5

Example 6 (#307 –diesel)

Catalyst:

A catalyst system according to the present disclosure was pre-prepared at room temperature in the following manner;

- 10 1) 40.03g (0.0709 moles) of didecyl dimethyl ammonium with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 2) 1.66g (0.00503 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by hand for 10 minutes.
- 3) 0.55g (0.00455) of H_3PO_4 (81%) was added to the mixture formed in 2) and gently
15 agitated by hand for 10 minutes.
- 4) 145.26g (2.135 moles) of 50% H_2O_2 was then added to 3).
- 5) The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 187.47g

- 20 The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst layer recovered was 49.56g.

25 **Oxidation**

A 2kg sample of transmix diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280 ppm sulphur and 8.29ppm nitrogen.

The sample was pre heated to $>60^\circ\text{C}$ and placed under the mixer.

- 0.12g of catalyst was added, followed by 2.97g 50% H_2O_2 . The solution was then
30 mixed for 30 minutes at 6000 rpm.

The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. An organic layer of recovered catalyst was then observed and removed. The oxidised diesel was then recovered and measured sulphur of 111.3 ppm.

5 A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This step was repeated a further 8 times.

10 After the fourth extraction (strip#4) the sulphur was measured at 15.53 ppm vs the baseline strip#4 of 16.12 ppm.

 Whilst multiple water washes were done on the baseline catalyst oxidation only 2 washes were carried out. The sample was then checked for sulphur and nitrogen. The sulphur was 4.66 ppm and nitrogen was 5.34 ppm. This surpassed the sulphur target of 10 ppm.

15

Figure 3

 Figure 3 depicts the initial reduction of sulphur in the diesel following oxidation from 280 ppm to 111.3 ppm. The reduction in sulphur confirms the migration of a certain amount of sulphur to the spent catalyst phase, reducing the mass sulphur load on the solvent extraction cycle. This is further reduced following x9 solvent extractions with water/NMP (0.5:1), with the sulphur content reaching 9.25 ppm. After two water washes, the sulphur content was reduced to 4.66 ppm.

20

Example 7 (#295B)

25 Preparation of DDAC/DDAHS mixture:

Step 1. 98.14g (0.300 moles) of 30% sulphuric acid and 110.84g (6.151) demineralised water was added to 267.8g (0.592 moles) of didecyl dimethyl ammonium chloride and mixed for 5 minutes.

Step 2. Another 862.25g (2.637 moles) of sulphuric acid was heated to 80°C for 2 hours on a heated magnetic stirrer with the heat maintained at 80°C in a refluxing glass apparatus.

30

The mixture was then cooled to 40°C and a further 199.97g (11.097 moles) of demineralised water was added. The mixture was heated to 40°C for 30 minutes on a heated magnetic stirrer with the heat maintained at 40°C in a refluxing glass apparatus. After 30 minutes a further 200.34g (11.118 moles) demineralised water was added and stirred for 30 minutes as per above.

Upon cooling the sample settle into two phases. 1207.75g of heavy aqueous phase was drained and measured pH <1. 522.04g of the light phase organic phase was recovered.

Step 2 was repeated.

The sample was left to settle for 2 days and was a stable emulsion. When aqueous phase was drained 592.38g of light phase organic phase was recovered. The organic phase contained the didecyl dimethyl ammonium with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride.

Catalyst

A catalyst system according to the present invention was pre-prepared at room temperature in the following manner;

- 1) 45.76g (0.0810 moles) of didecyl dimethyl ammonium with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 2) 2.42g (0.00734 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by hand for 10 minutes.
- 3) 0.86g of H_3PO_4 (81%) (0.00711 moles) was added to the mixture formed in 2) and gently agitated by hand for 10 minutes.
- 4) 236.85g (3.482 moles) of 35% H_2O_2 was then added to 3).
- 5) The solution formed in 4) was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 283.1g

The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst recovered was 66.29g.

Oxidation

A 2kg sample of the transmix diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280ppm sulphur and 8.29ppm nitrogen.

- 5 The sample was pre heated to $>60^{\circ}\text{C}$ and placed under the mixer.
0.24g of catalyst was added, followed by 5.32g 50% H_2O_2 . The solution was then mixed for 30 minutes at 6000 rpm.

- The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. An organic layer of recovered catalyst
10 was then observed and removed. The oxidised diesel layer was then recovered and measured sulphur of 134.8 ppm.

- A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel
15 sample were then separated under gravity. This step was repeated a further 5 times.

After strip #6 the sulphur was measured at 13.19 ppm vs the baseline strip #6 of 13.75 ppm.

Figure 4

- 20 Figure 4 compares the present sample with the baseline sample. It depicts the initial reduction of sulphur in the diesel sample following oxidation from 280 ppm to 134.75 ppm. This is significant compared to the baseline. The reduction in sulphur confirms the migration of a certain amount of sulphur to the spent catalyst phase, reducing the mass sulphur load on the solvent extraction cycle. This is further reduced
25 following x6 solvent extractions with water/NMP (0.5:1), with the sulphur content reaching 13.19 ppm.

Whilst multiple water washes were done on the baseline catalyst oxidation, no water wash was carried out in this Example.

- 30 **Example 8A** (#293 – Recycled catalyst)

Catalyst:

A catalyst system according to the present invention was pre-prepared at room temperature in the following manner:

- 1) 61.32g (0.109 moles) of didecyl dimethyl ammonium with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 5 2) 6.44g (0.0195 moles) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to 1) and gently agitated by hand for 10 minutes.
- 3) 2.29g (0.0189 moles) of H_3PO_4 (81%) was added to the mixture formed in step 2) and gently agitated by hand for 10 minutes.
- 4) 316.99g (3.262 moles) of 35% H_2O_2 was then added to the mixture of step 3).
- 10 5) The solution of 4) was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 381.47g

- The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst recovered was 101.69g.
- 15

i) 1st Oxidation

- A 2kg sample of transmix diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280ppm sulphur and 8.29ppm nitrogen.
- 20

The sample was pre heated to $>60^\circ\text{C}$ and placed under the mixer.

0.72g of catalyst was added, followed by 9.1g 35% H_2O_2 . The solution was then mixed for 30 minutes at 6000 rpm.

- The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. 1.3g of organic layer of recovered catalyst with a small amount of diesel was then observed and isolated. The oxidised diesel layer was then recovered and measured sulphur of 140.55 ppm to ASTM D5623.
- 25

1st Solvent extraction

- A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1
- 30

solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This step was repeated a further 3 times.

After strip#4 the sulphur was measured at 13.75 ppm vs the baseline strip#4 of 16.12 ppm. See Figure 5.

5

ii) 2nd Oxidation

A 2kg sample of diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280 ppm sulphur and 8.29 ppm nitrogen.

The sample was pre heated to >60°C and placed under the mixer.

10 1.3g of recovered catalyst from the first oxidation was added, followed by 9.27g 35% H₂O₂. The solution was then mixed for 30 minutes at 6000 rpm.

The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. 0.46g of organic layer of recovered catalyst with a small amount of diesel was then observed and isolated. The oxidised diesel

15 layer was then recovered and measured sulphur of 142.11 ppm.

2nd Solvent extraction

20 A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel sample were then separated under gravity. This step was repeated a further 4 times.

After strip #5 the sulphur was measured at 12.94 ppm vs the baseline strip#4 of 14.55 ppm. See Figure 6.

The water wash was done on the baseline only, not the above 2 examples.

25

Example 8B (#293) recycling and replenishing of catalyst:

Catalyst

A catalyst system of the present invention was prepared according to the methodology outline above in Example 7.

30

Oxidation

The oxidation process was carried out in a similar manner to that described in Example 7, wherein a 2kg sample of the transmix diesel with a sulphur content of 280ppm sulphur (to ASTM D5623) was contacted with 0.72g of catalyst and 35% H₂O₂ (3 x stoich).

5 An organic layer of recovered catalyst was then observed and removed. The oxidised diesel layer was then recovered and measured sulphur at 140.55 ppm. The observed catalyst layer was recovered for recycling. The oxidised diesel layer extracted using a mixture of 98% NMP and 2% demineralised water 6 times. The final sulphur content was measured at 13.75ppm.

10 The oxidation process was repeated by treating transmix (with sulphur content 280ppm) with the above recycled catalyst (recycled #1) and 35% H₂O₂ (3 x stoich). The oxidised diesel layer, measured sulphur at 142.11 ppm. Following extraction, as indicated above, the final sulphur content was 12.94 ppm.

The recovered catalyst was further recycled in further oxidation reactions with transmix diesel and topped up with fresh unused catalyst according to the following:

- Recycle #2 – no top up – oxidised diesel with sulphur 141.89ppm was reduced to 26.05 ppm sulphur following extraction;
- Recycle #3 – 0.4g top up -- oxidised diesel with sulphur 140.36 ppm was reduced to 11.74 ppm sulphur following extraction;
- 20 • Recycle #4 – 0.25g top up -- oxidised diesel with sulphur 135.96 ppm was reduced to 14.13 ppm sulphur following extraction;
- Recycle #5 – 0.19g top up -- oxidised diesel with sulphur 74.62 ppm was reduced to 15 ppm sulphur following extraction;
- Recycle #6 – 0.24g top up-- oxidised diesel with sulphur 138.94 ppm was reduced to 15.43 ppm sulphur following extraction.

25

The total amount of catalyst used across the 7 oxidations was 1.81g.

Note - The reduction of sulphur at oxidation prior to stripping with solvent extraction. It is believed that the sulphone is attracted to the catalyst which is removing a portion prior to stripping.

This Example demonstrates the effectiveness of recycling the recovered catalyst system and topping up the recovered catalyst system with a virgin catalyst system (that has not been recycled) for subsequent use in the oxidative desulphurization process.

5 **Example 9** (#312)

Preparation of Catalyst:

A catalyst system according to the present invention was pre-prepared at room temperature in the following manner:

- 1) 38.09g (0.0842 moles) of didecyl dimethyl ammonium chloride was measured in
10 a beaker.
- 2) 76.22g (0.233 moles) of 30% aqueous H_2SO_4 was added to 1).
- 3) 2g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.00606 moles) was added to 2) and gently agitated by hand
for 10 minutes.
- 4) 0.71g (0.00587 moles) of H_3PO_4 (81%) was added to the mixture formed in 3)
15 and gently agitated by hand for 10 minutes.
- 5) 137.86g (2.026 moles) of 50% H_2O_2 was then added to 4).

The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 251.62g

- 20 The sample was then decanted, with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst recovered was 65.4g.

25 **Oxidation**

A 2kg sample of transmix diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 280ppm sulphur and 8.29 ppm nitrogen.

The sample was pre heated to $>60^\circ\text{C}$ and placed under the mixer.

- 30 0.12g of catalyst was added, followed by 2.97g 50% H_2O_2 . The solution was then mixed for 30 minutes at 6000 rpm.

The stoichiometric ratio of moles of hydrogen peroxide to moles of sulphur is about 2.5:1.

The mixture was then decanted and cooled to room temperature. An aqueous phase was the heaviest phase and drained first. An organic layer of recovered catalyst
5 was then observed and removed. The oxidised diesel was then recovered and measured sulphur of 132.25 ppm

A sample of oxidised diesel was then extracted using a mixture of 98% NMP and 2% demineralised water. The extraction was done manually shaking the mixture at 0.5:1 solvent to hydrocarbon ratio at room temperature for 2 minutes. The solvent and diesel
10 sample were then separated under gravity. This step was repeated.

The final step was to remove residual solvent using a water wash. The demineralised water was added at a ratio of 0.05:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes. This step was repeated.

The sample was then checked for sulphur and nitrogen. The sulphur was 3.08 ppm
15 and nitrogen was 3.13 ppm

Example 10 (H₂O₂ addition as penultimate step)

Catalyst:

A catalyst according to the present disclosure was pre-prepared at room
20 temperature in the following manner;

- 1) 10.4g (0.0184 moles) of didecyl dimethyl ammonium chloride with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 2) 0.27g of Na₂WO₄·2H₂O (0.0008 moles) was added to 1) and gently agitated by hand for 10 minutes.
- 25 3) 39.52g (0.581 moles) of 50% H₂O₂ was then added to 2).
- 4) 0.07g (0.0006 moles) of H₃PO₄ (81%) was added to the mixture formed in 3) and gently agitated by hand for 10 minutes.

The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

30 Post mixing the mass was checked at 47.28g.

The preparation of the catalyst in this manner indicated that there was no rapid decomposition of the H_2O_2 prior to the addition of H_3PO_4 . Based on the unexpected stability and lack of observable rapid decomposition of hydrogen peroxide, it is anticipated that the catalyst prepared according to this methodology will be effective in the oxidative desulphurisation of hydrocarbon material containing sulphur.

Example 11(#329-Further extraction of recovered hydrocarbon)

Preparation of Catalyst:

Catalyst was pre-prepared at room temperature in the following manner;

- 1) 102.9g of DidecylDimethylAmmonium with an estimated anion ratio of 80% Hydrogen Sulfate to 20% Chloride was measured in a beaker
- 2) 5.41g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added and gently agitated by hand for 10 minutes.
- 3) 1.92g of H_3PO_4 (81%) was added to the mixture and gently agitated by hand for 10 minutes.
- 4) 72.86g of 50% H_2O_2 was then added.

The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 486.40g

- The sample was then decanted with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst recovered was 159.00g.

Oxidation

- A 1kg sample of diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was 4492 ppm sulfur.

The sample was pre heated to $>60^\circ\text{C}$ and placed under the mixer.

2.35g of catalyst was added, followed by 28.86g 50% H_2O_2 . The solution was then mixed for 30 minutes at 8000rpm.

- The mixture was then placed in a water bath at 35°C for 18 hours. When separated an aqueous phase was the heaviest phase. An organic layer of **recovered catalyst** was

then observed and removed. The oxidised diesel was then recovered. The sulphur level was measured at 3295.96 ppm.

A sample of oxidised diesel was then extracted using NMP. The extraction was done using a Silvertone L5M-A mixer for 6 minutes at 3000rpm using a solvent ratio of 3:1 at room temperature. The extraction step was repeated 8 more times.

The final step was to remove residual solvent using a water wash. The demineralised water was added at a ratio of 0.2:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes. This step was repeated once.

The sample was then checked for sulfur. The sulfur was measured at 8.31ppm.

The extract of the above solvent extraction was water washed to recover hydrocarbon. 4648g of water was added to 9293g of the extract at room temperature. The solution was then mixed for 6 minutes at 6000rpm. The mixture was left to settle overnight. 634g of diesel was recovered. The sample was then checked for sulfur. The sulfur was measured at 1577.13ppm.

The sample of recovered diesel was then extracted using NMP repeating the original solvent extraction procedure. The extraction was done using a Silvertone L5M-A mixer for 6 minutes at 3000rpm using a solvent ratio of 3:1 at room temperature. The extraction step was repeated 8 more times.

The final step was to remove residual solvent using a water wash. The demineralised water was added at a ratio of 0.36:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes.

The sample was then checked for sulfur. The sulfur was measured at 9.08ppm

The **extract** was water washed to recover hydrocarbon. 2207g of water was added to 4409g of the extract at room temperature. The solution was then mixed for 6 minutes at 6000rpm. The mixture was left to settle overnight. 343g of diesel was recovered. The sample was then checked for sulfur. The sulfur was 1359.11ppm

This example demonstrates that recovered hydrocarbon from the extract of the solvent extraction can successfully undergo further solvent extraction to extract sulphur.

Table 1 - Summary of Examples 1-11:

Example:	Fuel type	Feed sulphur content (ppm)	Sulphur content after oxidation (before extraction) (ppm)	Final sulphur content (ppm)	At strip # (solvent/water extraction)	Ratio of moles O:S
1 baseline #290	Diesel	280	235.8	16.12 13.75 11.285.95	Strip #4 Strip#6 Strip #13 terminal (x4w/wash)	5.6
2 #311	Diesel	280	132.25	3.19	solv x9 Terminal (x 1w/wash)	2.41
3 #301	Clarified Oil	15425	-	4377	N/A distillation terminal	1.47
4 #308	Heavy Fuel Oil (HFO)	11407	-	- 2043	Solv x6 Terminal (x1 w/wash)	2
5 #304	Diesel	483.1	258.54	6.52	Solv x9 Terminal (w/wash)	2.09
6 #307	Diesel	280	111.3	15.53 9.25 4.66	Strip #4 Strip #9 Terminal (x2w/wash)	2.36
7 #295B	Diesel	280	134.75	20.84 13.19	Strip #4 (5 in Fig 2) Strip #6 (7 in Fig 2)	5.39
8i #293A	i) Diesel	280	140.55	13.75	Strip #4	5.3
8ii #293B	ii) Diesel (recovered and recycled catalyst)	280	142.11	16.4 12.94	Strip #4 Strip #5	5.3
9 #312	Diesel	280	132.25	- 3.08	Solv x2 Terminal (w/wash x2)	2.5
11	Diesel (hydrocarbon recovery and	4492	3295.96	1 st - 8.31 2 nd - 9.98	Sol x9, w/wash x 2 Sol x 9, w/wash x1	3

	further extraction)					
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The high ratio of moles O:S in Examples 7, 8i and 8ii, was due to the inventors not wanting to compromise the catalyst performance by leaning out the peroxide. With continued experimentation the lower O:S ratios were considered and generally no further advantage has been observed when the ratio of moles O:S is increased to above 3:1.

5 The term “terminal” refers to the final sulphur content after the specified solvent extraction/water washing.

In addition to the above observations, the inventors surprisingly noted that desulphurisation reactions carried out with the catalyst system disclosed herein were highly reactive and effective in reducing the sulphur content immediately after the oxidation process before and prior to extraction. The notable advantages of this novel feature are:

- 1. A portion of the sulphur is carried from the system with spent catalyst, which is then sequestered in bitumen or other non-combustion application.
- 2. The post oxidation reduction in sulphur results in a reduced sulphur mass loading on the solvent extraction section of the process.

Example 12 - Comparison of Example 6 (#307) with preparation of prior art catalyst

In US 8,715,489 (Maritime *et al*), polyoxometallate catalysts are prepared by adding a dissolvable Group VIb metal (tungstate or molybdate) salt; a dissolvable salt of phosphorous, silicon, arsenic or boron; and a quaternary ammonium salt, to an aqueous hydrogen peroxide solution. This essentially involved the addition of the dissolvable Group VIb metal salt to the aqueous hydrogen peroxide solution, followed by the addition of the dissolvable salt of phosphorous, silicon, arsenic or boron to the hydrogen peroxide solution, followed by the addition of the quaternary ammonium salt to the hydrogen peroxide solution.

A comparison was made between Examples 1 in US 8,715,489 (Saudi ‘489) and Example 6 (Sample #307) of the present catalyst system. These results are summarised in the below Table 2.

Table 2 – Comparison of efficiency of catalyst system of present disclosure vs prior art

Saudi #489 Example 1 v Ultraclean #307				
Sulfur mass - 100ml, assumed SG 0.84, 910ppm ¹		0.07644 g	Ultraclean	
		50 mg	Ultraclean (#307)	Reduction
Catalyst ²		0.05 g	0.015422 g	69%
Quat ³	26%	0.013071 g	0.00442 g	66%
Na ₂ WO ₄ .2H ₂ O	35%	0.017254 g	0.000244 g	99%
H ₃ PO ₄ ⁴	15%	0.007488 g	0.0001 g	99%
100% H ₂ O ₂	24%	0.012187 g	0.010692 g	12%
	100%			
1. Sulfur mass based on assumed diesel density				
2. Assumed Catalyst Composition based on Input ratio (Excl H ₂ O)				
3. Assumes 100% Tetraoctylammonium chloride				
4. Saudi H ₃ PO ₄ concentration 85%, Ultraclean H ₃ PO ₄ 81%, both adjusted to 100%				

This indicates that the proposed catalyst system functions in a very efficient manner when compared with prior art. This is particularly the case for the transition metal component of the catalyst. Advantageously, the reduction in transition metal content in the catalyst has a beneficial environmental effect.

This advantage is in addition to the noted advantages of using the catalyst of the present disclosure in the oxidative desulphurisation process disclosed herein versus the baseline process which uses a catalyst prepared according to the prior art (cf US'489) as detailed in Table 1 (See #307 and #290). Notably, the significant reduction in sulphur levels immediately after oxidation for #307 compared to #290 indicates the highly reactive and effective nature of the catalyst disclosed herein when used in oxidative desulphurisation.

Example 13 - Reduction in Sulphur content and TAN (#324 – QOPT#10)

Preparation of Catalyst:

Catalyst was pre-prepared at room temperature in the following manner:

- 1) 102.9g (0.0182 moles) of DidecylDimethylAmmonium Chloride with an estimated anion ratio of 80% hydrogen sulphate to 20% chloride was measured in a beaker.
- 2) 5.5g (0.0167 moles) of Na₂WO₄.2H₂O was added and gently agitated by hand for 10 minutes.
- 3) 1.92g of H₃PO₄ (81%) (0.0157 moles) was added to the mixture and gently agitated by hand for 10 minutes.

4) 378.70g (5.567 moles) of 50% H₂O₂ was then added.

The solution was then mixed using a Silverstone L5M-A mixer at room temperature for 30 minutes.

Post mixing the mass was checked at 486.40g

5 The sample was then decanted, with a heavy aqueous phase and the organic catalyst being the light phase. The sample was left to settle under gravity in an open beaker for 48 hours. The aqueous phase was drained. The organic catalyst recovered was 159.00g.

10 Oxidation:

A 2kg sample of diesel was checked for sulphur and nitrogen to ASTM D5623. The sample was about 342 ppm sulphur and 35.9ppm nitrogen.

The sample was also checked for TAN to ASTM D974. The sample was 1.1 mg KOH/g.

15 The sample was pre heated to >60.deg.C and placed under the mixer.

0.27g of catalyst was added, followed by 6.78g 50% H₂O₂. The solution was then mixed for 30 minutes at 6000rpm.

The mixture was then placed in a water bath at 35°C for 48 hours. When separated an aqueous phase was the heaviest phase. An organic layer of recovered catalyst was
20 then observed and removed. The oxidised diesel was then recovered.

A sample of oxidised diesel was then extracted using NMP. The extraction was done using a Silverton L5M-A mixer for 6 minutes at 3000rpm using a solvent ratio of 0.5:1 at room temperature. The extraction step was repeated 14 more times.

The final step was to remove residual solvent using a water wash. The
25 demineralised water was added at a ratio of 0.1:1 water to diesel and shaken in a separatory funnel at room temperature for 2 minutes. This step was repeated once.

The sample was then checked for sulfur and nitrogen and TAN. The sulfur was 4.5 ppm and nitrogen was 15.4 ppm. TAN was <0.02mg KOH/g. This process advantageously provides a significant reduction in both sulphur content and TAN.

30 The steps, features, integers, compositions and/or compounds disclosed herein or indicated in the specification of this application individually or collectively, and any

and all combinations of two or more of said steps or features.

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CLAIMS:

1. A method of preparing a catalyst system, the method comprising combining one or more phase transfer catalysts (PTC), one or more metal oxides, one or more oxidants and one or more inorganic acids, wherein the method does not comprise combining the
5 oxidant and the metal oxide to form a mixture comprising the oxidant and the metal oxide unless the PTC and/or the inorganic acid are also present in the mixture.
2. A method of preparing a catalyst system according to claim 1, the method comprising combining the phase transfer catalyst (PTC) and one or more metal oxides; followed by addition of the oxidant and the inorganic acid.
- 10 3. The method of claim 1, wherein the PTC and the oxidant are combined followed by addition of the metal oxide and then addition of the inorganic acid.
4. The method of claim 2 wherein the oxidant is added last.
- 5 The method of claim 2 wherein the inorganic acid is added last.
6. A method of preparing a catalyst system, the method comprising
15 i) contacting an oxidant with a mixture comprising a phase transfer catalyst (PTC) and one or more metal oxides; followed by
ii) adding an inorganic acid to the mixture formed in i).
7. A method of preparing a catalyst system, the method comprising contacting an oxidant with a mixture comprising:
20 - a phase transfer catalyst (PTC);
- one or more metal oxide oxides; and
- an inorganic acid.
8. The method of claim 7 wherein the one or more metal oxides is combined with the PTC prior to combining with the inorganic acid.
- 25 9. The method of claim 7 comprising:
a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC;
b) adding the inorganic acid to the mixture of metal oxide and PTC followed by:
c) addition of the oxidant.
- 30 10. The method of claim 7 comprising:

- a) combining the one or more metal oxides and the PTC to form a mixture of metal oxide and PTC;
- b) adding the oxidant to the mixture of metal oxide and PTC followed by:
- c) addition of the inorganic acid.
- 5 11. The method of any one of claims 1-10 wherein the one or more metal oxides is one or more Group VIb metal oxides, preferably wherein the one or more metal oxide is selected from one or more of the following: tungstic acid, tungsten trioxide, tungstate salt including sodium tungstate, tungstate salt dihydrate including sodium tungstate dihydrate, molybdic acid, molybdic acid monohydrate, molybdic acid dihydrate,
- 10 molybdenum trioxide, molybdate salt including sodium molybdate, and molybdate salt dihydrate including sodium molybdate dihydrate.
12. The method of any one of claims 1-11 wherein the metal oxide is sodium tungstate dihydrate.
13. The method of any one of claims 1-12 wherein the inorganic acid is a
- 15 phosphorous containing inorganic acid.
14. The method of any one of claims 1-13 wherein the phase transfer catalyst (PTC) is selected from the group consisting of: quaternary ammonium salts; quaternary phosphonium salts; guanidinium salts, including hexaalkyl guanidinium salts; N-quaternized heterocyclic compounds, including pyridinium salts or imidazolium salts,
- 20 phosphazanium salts and linear or cyclic polyethylene glycols and their ethers, including cyclic crown ethers and cryptands, preferably wherein the phase transfer catalyst (PTC) is a quaternary ammonium salt, preferably wherein the phase transfer catalyst (PTC) is a quaternary ammonium salt selected from quaternary ammonium hydrogen sulphates, quaternary ammonium chlorides and quaternary ammonium
- 25 bromides.
15. The method of any one of claims 1-14 wherein the PTC is didecyl dimethylammonium hydrogen sulphate (DDAHS), didecyl dimethylammonium chloride (DDAC) or a mixture thereof; alternatively wherein the PTC is methyl tricaprylammonium hydrogen sulphate, methyl tricaprylammonium chloride or a
- 30 mixture thereof.
16. The method of claim 1-15 wherein the PTC is an aqueous solution.

17. The method of any one of claims 1-16 wherein one or more of the following conditions are met:

the one or more metal oxides is in an amount of 0.001 mole% of catalyst system to about 6 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system or about 0.3 mole% of catalyst system;

the inorganic acid is in an amount of about 0.001 mole% of catalyst system to about 6.0 mole% of catalyst system; or about 0.001 mole% of catalyst system to about 0.6 mole% of catalyst system; or about 0.01 mole% of catalyst system to about 0.6 mole% of catalyst system or about 0.3 mol% of catalyst system;

the PTC is in an amount of about 2.5 mole% of catalyst system to about 3.5 mole % of catalyst system; or about 3.0 mole% of catalyst system to about 3.3 mole % of catalyst system or about 3.2 mole % of catalyst system;

the oxidant used in preparing the catalyst system is in a molar ratio of oxidant to metal oxide in the range of about 7000:1 to 100:1; or about 7000:1 to 300:1 or about 500:1;

the molar ratio of metal oxide to PTC is in a range of about 0.5:1 to 0.0004:1; or about 0.18:1 to 0.005:1 or about 0.09:1; and/or

the molar ratio of PTC to metal oxide to inorganic acid to oxidant is in a range of about 0.032 : 0.0057 : 0.0055 : 0.96 to about 0.032 : 0.00015 : 0.00028 : 0.97 or about 0.032 : 0.0029 : 0.0028 : 0.96

18. The method of any one of claims 1-17 wherein the oxidant is about 20-70% aqueous hydrogen peroxide, or about 50% aqueous hydrogen peroxide.

19. The method of claim 1 wherein the oxidant is contacted with the mixture comprising PTC, one or more metal oxides and inorganic acid to form a reaction mixture comprising an oxidised catalyst mixture.

20. The method of claim 19, wherein the catalyst system is not further isolated from the oxidised catalyst mixture.

21. The method of claim 19 wherein a water-immiscible layer forms comprising the oxidised catalyst mixture, preferably wherein the water-immiscible layer is separated to form a separated water-immiscible layer.

22. A method of preparing a catalyst system, the method comprising the steps of:
- a) combining sodium tungstate dihydrate and an aqueous quaternary ammonium salt to form a metal oxide and quaternary ammonium salt mixture;
 - b) adding aqueous phosphoric acid to the metal oxide and quaternary ammonium salt mixture to form a reaction mixture; followed by
 - 5 c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst mixture;
 - d) allowing the oxidised catalyst mixture to settle to form multiple layers including a water-immiscible layer containing the catalyst system; and
 - 10 e) optionally separating the water immiscible layer containing the catalyst system.
23. The method of preparing a catalyst system according to claim 22, the method comprising the steps of:
- a) combining sodium tungstate dihydrate and aqueous didecyl
 - 15 dimethylammonium hydrogen sulphate (DDAHS) to allow dissolution of the sodium tungstate dihydrate in DDAHS to form a dissolved metal solution;
 - b) adding aqueous phosphoric acid to the dissolved metal solution; followed by
 - c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst solution;
 - 20 d) allowing the oxidised catalyst solution to settle to form 2 layers including a water-immiscible layer containing the catalyst system; and
 - e) optionally separating the water-immiscible layer containing the oxidised catalyst solution.
24. The method of preparing a catalyst system according to claim 22, the method
- 25 comprising the steps of:
- a) combining sodium tungstate dihydrate and a mixture of methyl
 - tricaprylammonium hydrogen sulphate and methyl tricaprylammonium chloride
 - dissolved or suspended in hydrocarbon (e.g. diesel) to form a reaction mixture;
 - b) adding aqueous phosphoric acid to the reaction mixture; followed by
 - 30 c) adding aqueous hydrogen peroxide and mixing to form an oxidised catalyst solution;

- d) allowing the oxidised catalyst solution to settle to form 3 layers including a water-immiscible layer containing the catalyst system; and
- e) optionally separating the water-immiscible layer containing the oxidised catalyst solution.
- 5 25. A catalyst system prepared by the method of anyone of claims 1-24.
26. The catalyst of claim 25 for use in a process of desulphurising a hydrocarbon material containing sulphur.
27. A process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds, the process comprising:
- 10 a) contacting the hydrocarbon material containing sulphur compounds with hydrogen peroxide and the catalyst system prepared by the method of any one of claims 1-24, so as to oxidise at least a portion of the sulphur compounds in the hydrocarbon material to form an oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and
- 15 b) separating at least a portion of the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with a reduced sulphur content.
28. The process of claim 27 wherein the catalyst system is added to the hydrocarbon material followed by addition of the hydrogen peroxide.
- 20 29. The process of any one of claims 27-28 wherein the catalyst system is prepared and used in the process *in situ*.
30. The process of any one of claims 27-29 wherein one or more of the following conditions are met:
- the molar ratio of hydrogen peroxide to sulphur in hydrocarbon material
- 25 containing sulphur compounds is in a range of about 2:1 to about 5:1 or about 2:1 to about 2.5:1.
- the molar ratio of hydrogen peroxide to sulphur in hydrocarbon material containing sulphur is a about 2.5:1.
- the mass ratio of catalyst system disclosed herein to sulphur in hydrocarbon
- 30 material containing sulphur (catalyst:S) is about 0.2:1.

31. The process of any one of claims 27-30 wherein the at least a portion of the oxidised sulphur compounds is separated from the oxidised hydrocarbon mixture by solvent extraction to provide a raffinate comprising the hydrocarbon material with reduced sulphur content and an extract comprising the oxidised sulphur compounds.
- 5 32. The process of claim 31 wherein the solvent extraction is carried out with a first extraction solvent selected from the group consisting of N-methyl pyrrolidone (NMP), acetonitrile, DMF, DMSO, methanol, water, brine, furfural and an ionic liquid solution or mixtures thereof, preferably wherein the first extraction solvent is a mixture of N-methyl pyrrolidone and water (aqueous NMP), preferably as a mixture of about 98% N-
- 10 methyl pyrrolidone and 2% water (2% aqueous NMP).
33. The process of claim 32 wherein the process further comprises contacting the extract comprising the oxidised sulphur compounds with a second extraction solvent to form a second extract.
34. The process of claim 33, wherein the process further comprises separating at
- 15 least a portion of a hydrocarbon material from the second extract to form a second further hydrocarbon material and a second extract depleted of hydrocarbon material.
35. The process of claim 34, wherein the process comprises combining at least a portion of the second further hydrocarbon material with the oxidised hydrocarbon mixture comprising oxidised sulphur compounds prior to step b) of claim 27.
- 20 36. The process of any one of claims 34-35, wherein the process further comprises separating at least a portion of the first extraction solvent and/or the second extraction solvent from the second extract depleted of hydrocarbon of claim 34 to form one or more separated extraction solvent streams and a residue stream.
37. The process of claim 39, wherein the process further comprises separating at
- 25 least a portion of the hydrocarbon material from the residue of claim 39 to form a light hydrocarbon stream and a second residue.
38. The process of any one of claim 27-37 wherein the raffinate comprising the hydrocarbon stream with reduced sulphur content is washed with an aqueous solution including water and brine to form a washed hydrocarbon with reduced sulphur content
- 30 and a washate.
39. The process of any one of claims 27-38 the process comprises

contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system with stirring or agitation to provide the oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and

allowing the oxidised hydrocarbon mixture to settle to provide three layers
5 comprising i) an aqueous layer, ii) a hydrocarbon layer containing the oxidised sulphur compounds, and iii) a layer containing the catalyst system.

40. The process of any one of claims 27-38 the process comprises
contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system with stirring or agitation to provide the
10 oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and
allowing the oxidised hydrocarbon mixture to settle to provide two layers comprising i) an aqueous layer, ii) a layer containing hydrocarbon, the oxidised sulphur compounds, and the catalyst system.

41. The process of any one of claims 27-38 the process comprises
15 contacting the hydrocarbon stream containing sulphur compounds with hydrogen peroxide and the catalyst system with stirring or agitation to provide the oxidised hydrocarbon mixture comprising oxidised sulphur compounds; and
allowing the oxidised hydrocarbon mixture to settle to provide a mixture comprising hydrocarbon, the oxidised sulphur compounds, and the catalyst system.

20 42. The process of any one of claims 39-40 wherein the layer containing the catalyst system is separated to provide a recovered catalyst system, preferably wherein the recovered catalyst system is recycled as a catalyst system in a further oxidative desulphurisation process

43. The process of claim 41 wherein the catalyst system is separated to provide a
25 recovered catalyst system, preferably wherein the recovered catalyst system is recycled as a catalyst system in a further oxidative desulphurisation process.

44. A process of recycling the catalyst system used in the process of reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to any one of claims 27-43.

45. An apparatus for reducing the sulphur content of a hydrocarbon material containing sulphur compounds according to the process of any one of claims 28-48, the apparatus comprising:

- a) one or more oxidation reactors for oxidising at least a portion of the sulphur compounds in the hydrocarbon material containing sulphur compounds in the presence of the hydrogen peroxide and the catalyst system to provide the oxidised hydrocarbon mixture comprising hydrocarbon material, oxidised sulphur compounds and catalyst system;
- b) one or more vessels for delivering the hydrogen peroxide and the catalyst system to the oxidation reactor;
- c) a means for separating the oxidised sulphur compounds from the oxidised hydrocarbon mixture to provide a hydrocarbon material with reduced sulphur content;
- d) a means for separating the hydrocarbon stream with reduced sulphur content;
- e) a means for separating the catalyst system;
- f) one or more mixers for mixing the hydrocarbon material with reduced sulphur content with an extraction solvent to extract oxidised sulphur compounds into the extractant; and
- g) means to separate the hydrocarbon material with reduced sulphur content.

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